Studies On Halogenation Of Fatty Acids

THESIS (Resume)

Submitted To The Aligarh Muslim University

FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

HARNANDAN SINGH

1966

T 622

R E S U M E

The recent extension of the application of Friedal-Crafts reaction in introducing alkyl or acyl groups to aliphatic and alicyclic compounds in addition to benzene ring has increased the importance of alkylating and acylating agents in the study of organic reactions. From the view point of convenience, alkyl and acyl halides have been respectively used as the alkylating and acylating agents. In view of its use as an important acylating agent, several methods have been tried for the preparation of acyl chloride. It is however, readily obtained in a pure form by refluxing the acid with thionyl chloride. But the yield is always very poor.

A survey of the literature shows that though the poor yield of acyl chloride in the above method of its preparation has always been the problem, the reason has not been properly worked out. Secondly the the mechanism of fatty acid-thionyl chloride reaction is not definitely known, although the parallel reaction with alcohol has been thoroughly investigated and understood. It was in this perspective that this problem was investigated.

The kinetics of fatty acid-thionyl chloride reaction in solution was studied in detail. Thionyl chloride solution was pipetted in the reaction vessel which had a mercury seal, a spoon which contained the solution of the acid and an out-let. The acid solution was added to the thionyl chloride solution just by rotating the spoon and the stirrer was started simultaneously. The effluent gases were collected in a water jacketted gas-burette after passing them through a condenser. Water from the reaction bath was circulated through the jacket and the effluent gases were collected at the reaction bath temperature. Double burette gas assembly connected to the condenser through a three way stop-cock was used to collect and measure the amount of gases evolved in a definite interval of time. The concentration of the reactants was calculated from the amount of the gases evolved assuming that the reaction is simple.

$$R\ COOH + SOCl_2 = R\ COCl + SO_2 + HCl$$

The results may be summarized as follows:

(i) The reaction rate falls with the dissociation constant of the acid.

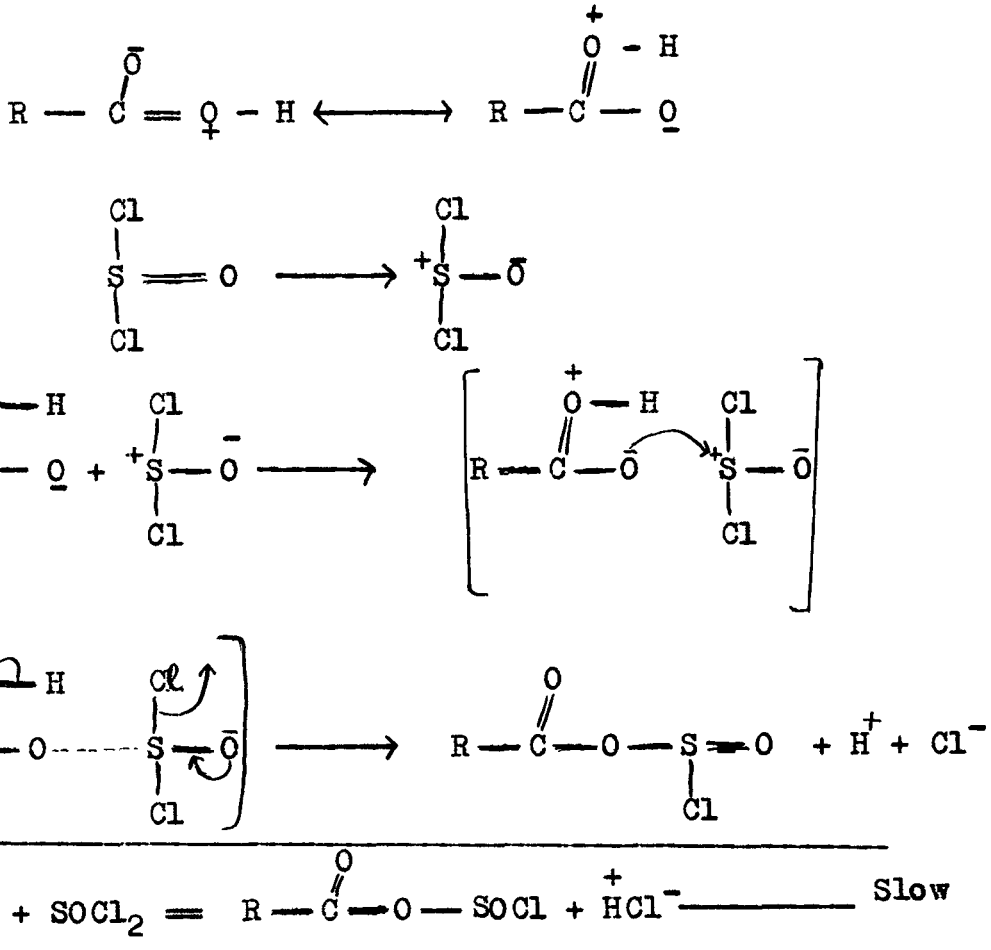
(ii) However, the result with substituted acetic acid is not so simple. The introduction of an electron

withdrawing group or atom like halogen, lowers the rate inspite of increasing its acidity. So much so that with trichloroacetic acid the reaction does not occur at all. The introduction of an electron releasing group, however, follows the general trend.

(iii) The rate rises with the dielectric constant of the medium.

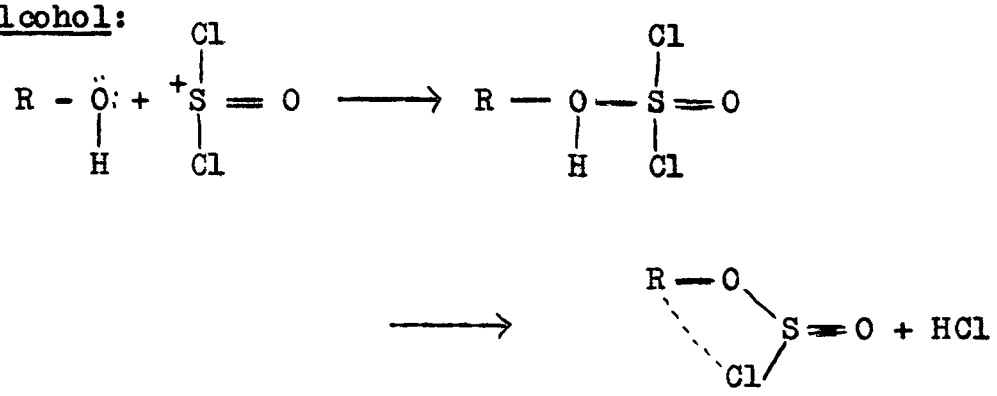
These facts suggest that the formation of chlorosulphite from unionised species is the rate determining step.

<u>Acid:</u>

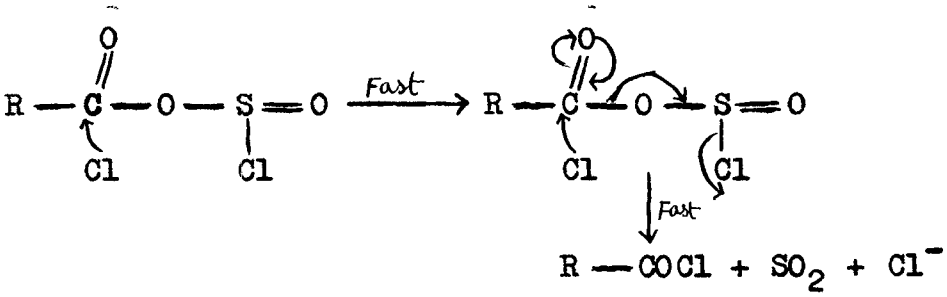


$$R\text{-}COOH + SOCl_2 = R-C(=O)-O-SOCl + H^+Cl^- \quad \text{(Slow)}$$

Alcohol:



This chloride ester differs from that of alcohols in the sense that the electron of S - Cl bond in the latter is pulled towards chlorine, whereas that of the former is pulled towards sulphur. Hence the intramolecular attack of chlorine of the ester on the carbonyl carbon of this ester through a cyclic intermediate is less probable. In view of this the attack by the free chloride ion seems more plausible.

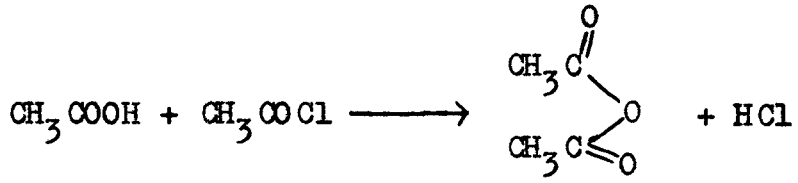


(iv) In each case, the reaction follows second order kinetics in the beginning but shows strong autoinhibition afterwards.

(v) The analysis of the effluent gases showed that HCl and SO_2 are evolved in equimolar proportion so long

as the reaction follows the second order kinetics. In the latter part of the reaction. However, the percentage of hydrogen chloride in the effluent gases increases with time.

(vi) The increase in the proportion of HCl in the effluent gases suggests that the slow reaction between acetic acid and acetyl chloride,



assumes importance in the latter part of the reaction.

(vii) In presence of acetic anhydride (added from out side) the autoinhibition started right from the beginning and the percentage of HCl in the effluent gases was also more than fifty from the start itself.

(viii) It was further found that the inhibitory effect of dioxane, which has a much higher electron density on its oxygen as compared to that of anhydride, is much more.

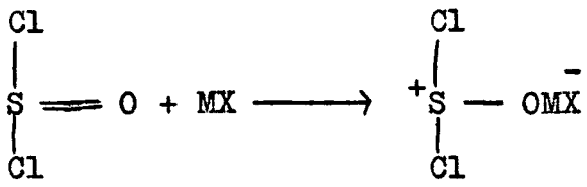
(ix) The values of thermodynamic functions $\Delta F^{\ddagger}$ & $\Delta S^{\ddagger}$ in different solvents are almost the same but not so in xylene-dioxane mixtures. Although the dielectric

constant of xylene ($\mathcal{K}$ = 2.4) and dioxane ($\mathcal{K}$ =2.209) are almost the same, the rate falls appreciably with the rise in the proportion of dioxane. The entropy of activation $\Delta S^{\ddagger}$, however, rises with the proportion of dioxane in the mixture and assumes a somewhat constant value after fifty percent. In view of the polar nature of the reactants and the activated complex both are likely to be solvated in dioxane. The rate in presence of dioxane may, however, fall presumably due to strong solvation of the reactants.

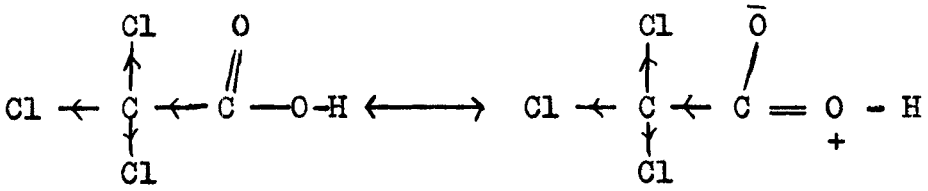
During this investigation, it was found that acetic acid-acetyl chloride reaction is not influenced by the dielectric constant of the medium, whereas the main reaction goes much faster in solvents of higher dielectric constant. It was thus considered that the yield of acyl chloride formation could be raised by reacting thionyl chloride and the acid in a solvents of high dielectric constant. The experiments upheld this view point. The yield was, however, raised further by performing the reaction at higher temperature in presence of alkali halide.

According to Krafts and Katiskiana the catalyst (alkali halides) enhances the concentration of the acid anion by forming salt of the acid and thereby increase the rate. With this mechanism one would, however, find it difficult to explain why the reaction with trichloro

acetic acid which is a very strong acid does not proceed at all without catalyst. Secondly why does fused sodium acetate not catalyse the reaction. In view of the modern approach of Friedel- Krafts acylation, it seems plausible to suggest that alkali halides form a coordination complex with thionyl chloride.



The reaction of positive charge on the sulphur atom in the complex, makes its binding with the oxygen of the carboxyl group quite facile which is not possible otherwise in case of trichloroacetic acid due to the strong pull on the electron of the oxygen of the carboxyl group.



Studies On Halogenation Of Fatty Acids

THESIS

Submitted To The Aligarh Muslim University

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

HARNANDAN SINGH

1966

A C K N O W L E D G E M E N T

I gratefully acknowledge my indebtedness to my teacher, Dr. M.A. Beg, D. Phil (Alld.), under whose guidance this work was carried out. I am also thankful to Prof. A.R. Kidwai, M.S.(Illinois), Ph.D.(Cornell), Head of the Chemistry Department for providing facilities and his keen interest during the progress of this work.

Thanks are also due to Dr. W. Rahman, M.Sc., Ph.D.(Alig.), Reader in Organic Chemistry section for helpful discussion.

I am very much indebted to the Council of Scientific and Industrial Research (India) for a fellowship.

Harnandan Singh

C O N T E N T S

Page No.

Page No.

Studies on the production of alkyl chlorides and acyl halides date back to 1801 when Barse[1-8] prepared alkyl chlorides of ethyl and methyl alcohols by the action of gaseous hydrochloric acid and zinc chloride[9] on the respective alcohols. Pierse and Puchot[10] preferred the use of phosphorous pentachloride and prepared several other alkyl chlorides.[11-24] Later on Villier[25], Kraft and Stauffer[26] prepared acyl chlorides by the action of phosphorous pentachloride on fatty acids. Since then a large number of acyl chlorides using different halogenating agents have been prepared. The word halogenation is usually employed for the replacement of a hydrogen atom by a halogen. The replacement of hydroxyl group of alcohols by a halogen atom has been frequently called halogenation[27,28,29]. Since in fatty acids thionyl chloride reaction[30] too, it is the hydroxyl of the carboxylic group that is replaced by chlorine hence the process has been called chlorination. A survey of the litrature shows, that though extensive work has been done on the preparatory aspect of acyl chlorides the kinetics of the process has been completely neglected.

From the results of Railton[31], Menschutkin[32], Schiff[33], Welchehaus[34], Chambon[35], Geunter[36], Kowalewesky[37],

Toroschenko[38], Melobendzki and Sachnowski[39], and Balarew[40]; Gerrard[41] concluded that the reaction of alcohols with phosphorous trichloride is as follows:

(1) $3ROH + PCl_3 \longrightarrow PCl_2OR + HCl$

(2) $P(OR)_3 + HCl \longrightarrow P(OH)(OR)_2 + RCl$

Later on Gerrard[42] stated that the reaction of (+β) actanol and ethyl mandelate with PCl_3 takes place as under:

$$PCl_3 + 3ROH \longrightarrow P(OR)_3 + 3HCl \longrightarrow P(OR)_2.OH + RCl$$

Gerrard and Phillips[43] proposed the following course for this reaction with PCl_5.

$$ROH + PCl_5 \longrightarrow ROPCl_4 + Cl^-H^+$$

$$ROPCl_4 + ROH \xrightarrow[-HCl]{} \begin{matrix} RO \\ RO \end{matrix}\!\!>PCl_3 \longrightarrow Cl^- + (RO)_2PCl_2^+ \longrightarrow RCl + ROPOCl_2$$

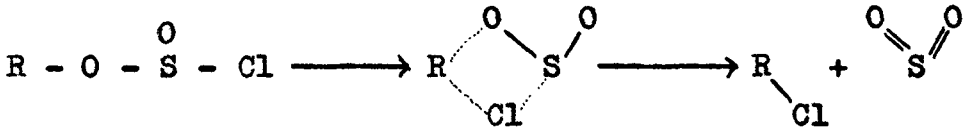
$$\begin{matrix} RO \\ RO \end{matrix}\!\!>PCl_3 \xrightarrow[-HCl]{ROH} (RO)_3PCl_2 \longrightarrow Cl^- + (RO)_3PCl^+ \longrightarrow RCl + (RO)_2POCl_2$$

This scheme was backed by the isolation of the final chloride esters. The other chloride esters could not, however, be isolated.

When phosphorous chlorides are replaced by thionyl chloride, the reaction of hydroxy-compounds takes a vigorous course. Voss and Blanke[44] obtained chlorosulphite to an yield of 68% by adding alcohol to thionyl chloride in cold, whereas Stahler and Schrim[45] could raise the yield to 85%

just by mixing the reactants in the reverse order. Carre and Libermann[46] prepared the chlorosulphites of primary alcohols in still higher yield but they failed to prepare the chlorosulphites of secondary alcohols. Gerrard[47] prepared the chlorosulphites of primary alcohols in excellent yield using thionyl chloride and could also extend the method to get a fair yield of sec-butyl chlorosulphite.

Hughes, Ingold and co-workers[48] have proposed that from alcohol and thionyl chloride, chlorosulphite is formed as a result of the establishment of carbon-chlorine bond with the simultaneous ejection of hydrogen chloride. The chlorosulphite later on decompose mono-molecularly to give sulphurdioxide and acyl chloride. The chlorocarbonates[27] were obtained in an analogous way by the interaction of alcohols and thionyl carbonate. Later on the formation of this intermediate chlorosulphite and its presumed decomposition through a cyclic transition



was varified by isolating the intermediate and studying its decomposition. The effect of solvents of different nature on the kinetics and stereochemistry of alkyl chloride formed from the decomposition of secondary alkyl

chlorosulphite has been studied by Lewis and Boozer[49]. The steric effects vary from clear retention in dioxane to complete inversion in toluene.

A similar type of process is said to be operative in fatty acid-phosphorous halide system. Although several individual higher acid chlorides were previously prepared by the action of phosphorous pentachloride on acids[25,26,50] the first comprehensive study of their preparation using this reagent was undertaken by Kraft and Burger[51] who prepared the higher acid chlorides by warming a equimolar mixture of the acid and phosphorous pentachloride. The action of phosphorous pentachloride on the higher acids has since been employed for the preparation of the acid chlorides of a number of saturated and unsaturated acids.[52,53,54] Although phosphorous pentachloride is, in many instances, a satisfactory reagent for preparating higher acid chlorides, its use sometimes presents certain difficulties. Its extremely high chemical reactivity often brings about secondary reactions that are not usually encountered with other halogenating agents. And it is frequently very difficult to separate the resulting phosphorous chloride completely from the acid chloride. Phosphorous trichloride is the most useful reagent for the preparation of higher acid chlorides. Phosphorous acid which is formed in this case being insoluble in higher acid

chlorides, sinks to the bottom of the reaction vessel and is easily removed. The mechanism of these reactions is similar to those of alcohols and according to Packer[55], phosphorous chlorides react with acids as under:

$$3R.CO.OH + PCl_3 \longrightarrow 3R.CO.Cl + P(OH)_3$$

$$R.CO.OH + PCl_5 \longrightarrow R.CO.O.Cl + HCl + POCl_3$$

In case of higher acids however, these reactions have been suggested to pass through the intermediate phosphite.[56]

$$R_3\text{-}C\text{-}C(=O)\text{—}OH + PCl_5 \xrightarrow{-HCl} R_3C\text{-}C(=O)\text{——}OPCl_4 \longrightarrow R_3CC(=O)\text{—}Cl + POCl_3$$

$$R\text{-}C(=O)\text{—}OH + PCl_3 \xrightarrow{-HCl} R\text{-}C(=O)\text{—}OPCl_2 \longrightarrow R\text{-}C(=O)\text{—}Cl + POCl.$$

Thionyl chloride generally gives better yields. Hence in usual practice, thionyl chloride is more frequently used to prepare acid chlorides. It readily converts saturated and unsaturated acids and also halo-substituted acids to the corresponding acid chlorides. Hoffmann[57] prepared iodo acetyl chloride by the action of thionyl chloride on iodo acetic acid. Mc Master and Ahmann[30] prepared acid chlorides of fatty acid series by refluxing the acid with excess thionyl chloride. In some cases, specially with dibasic acids, they reported the formation of acid anhydrides. When the acid is insoluble in $SOCl_2$, halogenation is effected in innert solvents like benzene.[30]

Adam and Ulich[58] obtained acid chlorides in

quantitative yield using oxalyl chloride. Later on Von Drop and Von Drop[59] obtained fumaryl chloride by the action of phthalyl chloride on fumaric acid. Lately Kyrides[60] extended this method and reported the preparation of butyryl chloride in 90% yield. Further acetyl chloride[61] has been prepared by the action of chloro-acetyl chloride on acetic acid. The high cost and the poor stability of these reagents, preclude their adoption as a general procedure.

Brown[62] prepared several acid chlorides using thionyl chloride as the halogenating agent. A stream of hydrogen chloride when passed through the reaction mixture, slightly increased the yield. Waser[63] prepared sebacyl chloride by the action of thionyl chloride on sebacicacid. Acid chlorides have also been prepared[64] by the action of sulphur and chlorine on the anhydrous soape of the corresponding fatty acid. Some of the old workers prefered silicon tetrachloride for the preparation of lower fatty acid chlorides. Rauter[65] prepared butyryl chloride by heating butyric acid with the reagent. Monotonna[66] prepared the acid chlorides of the several lower aliphatic acids using this reagent in an innert solvent. Hochsteller[67] obtained acid chlorides of lower fatty acids by passing acid vapours over phosgine or treating the sodium salt of the corresponding acid with

phosgene. Lauryl, palmityl, stearoyl chlorides were obtained[68] by the action of phosgene on the corresponding acids. Oleic acid chloride could not be obtained in better yield in either way. It was postulated that the reaction proceeds with the initial formation of an anhydride.

From the foregoing pages it is evident that a number of procedures have been suggested and investigated for the preparation of fatty acid chlorides. The above studies are however, lacking in many respects, viz., the solvent effect, catalytic effect, temperature effect and above all the kinetics of the process has not been given due consideration.

Recently Kraft[69] and Katiskiana reported what they called cationic catalysis by alkali chlorides in the production of substituted acid chlorides by thionyl chloride. In presence of pyridine, thionyl chloride reacts with fatty acid to give either acid chloride or anhydride[70], depending upon the proportion of the reactants used. Gerrard and Thrush[71] reported that addition of thionyl chloride (0.5 mol) to an ethereal solution of acetic acid (1 mol) and pyridine (1 mol) gave 97% acetic anhydride. They proposed the following mechanism for the formation of anhydride.

$$R.C\overset{+}{O}\overset{-}{O}H\ NC_5H_5 + SOCl_2 \longrightarrow R.COCl + C_5H_5N,\ SO(OH)Cl$$

$$R.C\overset{-+}{O}OH\ NC_5H_5 + RCOCl \longrightarrow (R.CO)_2O + C_5H_5N,\ HCl$$

Valuable information regarding reaction mechanism of organic reactions has come from the study of solvent effect on reaction rate. According to Hughes and Ingold[72], an increase in the ion-solvating power of the medium will accelerate the creation and concentration of charges on the transition complex. Therefore, the rate of these, as well as those of ionising reactions will be increased by an increase in the ion-solvating power of the medium. On the other hand, reactions between oppositely charged ions as well as those in which charge is on one atom in the reactants but spreads out over several in the transition state will go slower in a better ion-solvating solvent. The reaction between amines and alkyl halides has been studied in different solvents, and although numerous attempts have been made to establish relationships between reaction velocity and some physical property of the solvents, these have met with little sucess[73]. Evans and Jenkins[74], recognised that solvents effect the velocity coefficient in at-least two variable ways, (1) the probability factor (P), (2) the activation energy (E) of the kinetic equation

$$k = Pz\ e^{-E/RT}$$

The importance of P & E in solvent influence on reaction rate has also been discussed by Ingold and Nathan[75] with a reference to hydrolysis of saturated

benzoic esters. La Mer & Meller[76] studied the effect of solvent and the influence of temperature dependence on the dealdolization reaction.

Evans and Jenkins (loc.cit) have reported the following relation between the activation energies of reactions in solution and the dielectric constant of the medium

$$E = E_A + E_B/\epsilon$$

where E is the activation energy, ϵ is the dielectric constant of the medium, E_A and E_B are constants. However, Hinshelwood[77] et.al. have suggested that the activation energy is made up of two factors, the bond energy and the repulsion energy. Of the two factors which contribute to the activation energy, the bond-stretching energy (although altered by the presence of a substituent[78]), within certain limits, is independent of the solvent invironment. On the other hand the magnitude of the repulsion energy would be expected to be governed by the dielectric constant of the medium. The extent to which E varies with solvent depends upon the ratio of repulsion to activation energy (E_R/E).

In certain cases the repulsion energy is too small a fraction of the total activation energy to allow a material change in E with a change in the solvent. The decomposition of nitrogen pentoxide[79], in different solvents are the handy examples.

Fairclough and Hinshelwood[80] have reported that the constants P and E of the Arrhenius equation

$$k = Pz\ e^{-E/RT}$$

are not independent, and exhibit a close functional dependence in the variation of rate as a result of change in medium. In the alkaline hydrolysis of ethyl benzoate when the medium is gradually changed from aqueous acetone to aqueous alcohol[81], the values of E change regularly with the composition of the solvent and log Pz increases almost linearly with E.

Solvation[82] is another important aspect that determines the rate. Solvation of the activated complex brings about a decrease in the activation energy and a corresponding increase in the reaction rate, whereas, solvation of the reactants affects the activation energy and the reaction rate otherwise. However, if both the reactants and the activated complex are equally solvated, there may be little change in the activation energy, and the reaction rate.

Moelwyn-Hughes and Hinshelwood[83] observed that the bimolecular combination of triethylamine and ethyl iodide and the reaction between acetic anhydride and ethyl alcohol are slower in solution as compared to gas phase. They attributed the slowness of the reactions in solution to the nature of the reacting molecules and

not to the solvent deactivation. Later on this view was suported by Thompson and Blandon's[84] observations on the addition of methyl iodide to pyridine in solution.

Polar substituents in the reactants exert profound influence on the activation energy[85], and therefore, even apart from questions like catalysis and deactivation by the solvent molecules, the external field of the solvent molecules can very well exert a similar though a much smaller effect. Pickels and Hinshelwood[86] studied the influence of solvents on the velocity of pyridine-methyl iodide reaction and on that of benzoylation of m-nitroaniline, and reported that for non active solvents, the activation energy varies systematically with log k. In polar solvents, however, the variation is only in P and not in E.

One obvious function of the solvent molecules is to remove the energy from the activated complex and thus prevent it from reverting back into reactants. In such a case, P would be a direct measure of the efficiency with which the solvent molecules fulfil the function.[87] Although collision theory failed to explain the solvent effect on dealdolization La Mer and Miller (loc. cit) could explain it in terms of change in energy of activation. It has, however, been found useful to study the solvent effect in terms of activation parameters such

as free energy of activation ($\Delta F^{\ddagger}$), the internal energy of activation ($\Delta E^{\ddagger}$) and the entropy of activation ($\Delta S^{\ddagger}$). According to Eyring equation it is clear that it is the free energy of activation, and not the energy of activation, that determines the rate of a chemical reaction. Useful information regarding the nature of the transition complex can be obtained from the study of solvent effect on reaction rate with the help of the relation

$$\Delta F^{\ddagger} = \Delta E^{\ddagger} - T \Delta S^{\ddagger}$$

which follows directly from the Eyring equation. The entropy of activation for trimethylamine-ethyl bromide reaction is -43.3 E.U. in acetone and -50.1 E.U. in benzene. This difference is because the activated complex being polar in nature is solvated in acetone but not in benzene. The decarboxylation of malonic acid in various solvents gives activation parameters falling on two parallel lines. The upper line contains points for nine carboxylic acids, the lower line for a series of seven primary and secondary alcohols. Since carboxylic acids exist largely in the form of highly stable cyclic dimers, it is not surprising that they differ from other hydroxylic solvents in their solvation mechanisms.

Inductive effect has been the other useful tool

in elucidating the mechanism of organic reactions[90-95]. Although several references[96-98] are available for the preparation of substituted acid chlorides, no attempt seems to have been made regarding either the systematisation of their preparation or the application of inductive effect in elucidating the mechanism.

The kinetics of carboxylic acid-thionyl chloride system was taken up for the first time in 1953 by Gerrard and Thrush[99]. The progress of the reaction was followed by dissolving the effluent gases in caustic soda solution and estimating it gravimetrically. The rate was found to depend on the nature of the acid. They suggested the reaction through chlorosulphite, which readily decomposes to acyl chloride and sulphurdioxide. The work could not, however, been extended probably due to extremely tedious experimental procedure. In view of the wide application of thionyl chloride in preparing acyl chlorides and the incomplete knowledge of the process both from practical and theoretical view point, it was considered worthwhile to study fatty acid-thionyl chloride system in detail. Acyl chlorides of acids insoluble in thionyl chloride have been prepared (loc.cit) by mixing the reactants in an innert solvent; hence for generality sake I have studied this reaction in solution. Although the main emphasis of this work is on establishing

the mechanism of the process, the practical aspect has not been overlooked. The work described in this thesis deals with some such problems and includes the following studies:

(i) Kinetics of interaction of earlier members of fatty acid and thionyl chloride.

(ii) Solvent influence on fatty acid-thionyl chloride system.

(iii) Evidence for the side reaction giving acetic anhydride.

(iv) Establishment of the optimum condition (temperature, solvent, and catalyst) for the preparation of acyl chloride by thionyl chloride.

C H A P T E R - I

Purification of Reagents

All the reagents and the solvents employed in this investigation were purified before use.

Thionyl Chloride[100]

Commercial thionyl chloride frequently contains traces of inorganic acids and some other impurities. Thionyl chloride was first fractionated, in an all glass assembly from quinotine in order to remove acid impurities (50 gms. of thionyl chloride mixed with 10 ml. of quinoline). The receiver was protected from moisture by anhydrous calcium chloride tube. The distillatewas then refractionated as before from boiled linseed oil (50 gm distillate mixed with 20 ml. of linseed oil), the fraction between 76-78°C was collected.

Acetic Acid[101]

B.D.H. (L.R.) glacial acetic acid was frozen in ice at 16°C. The solid glacial acetic acid was

then dried with filter paper and distilled in quick-fit assembly. The distillate at 115°C was collected in a receiver carrying anhydrous calcium chloride tube. This acid was stored in dry bottles, kept over anhydrous calcium chloride in a desiccator.

Propionic Acid

Propionic acid (E. Merck) was distilled in an all glass assembly. The fraction between 139 - 140°C was collected in a receiver carrying an anhydrous calcium chloride tube. The acid so obtained was kept over anhydrous calcium chloride in a desiccator.

Benzene[10.2]

Commercial benzene contains impurities like thiophenes and water which can not be separated by distillation or by fractional crystallisation. To remove these impurities benzene was treated as follows:

Taking advantage of the fact that thiophene is more readily sulphonated than benzene, thiophene was removed from benzene by shaking it with conc. H_2SO_4. The technical benzene is shaken repeatedly with 15% of its volume of conc. H_2SO_4 in a glass stoppered separating funnel until the acid layer was colourless or very pale yellow on standing or until the thiophene test was negative.

After each shaking (lasting a few minutes), the mixture was allowed to settle and the lower layer of acid was drawn off. To remove most of the acid; benzene was shaken twice with water, then with 10% of sodium carbonate solution; and finally with water. It was then dried over anhydrous calcium chloride, filtered and distilled. The fraction between 80-81°C was collected. To free this fraction completely from water, sodium wire was introduced in it.

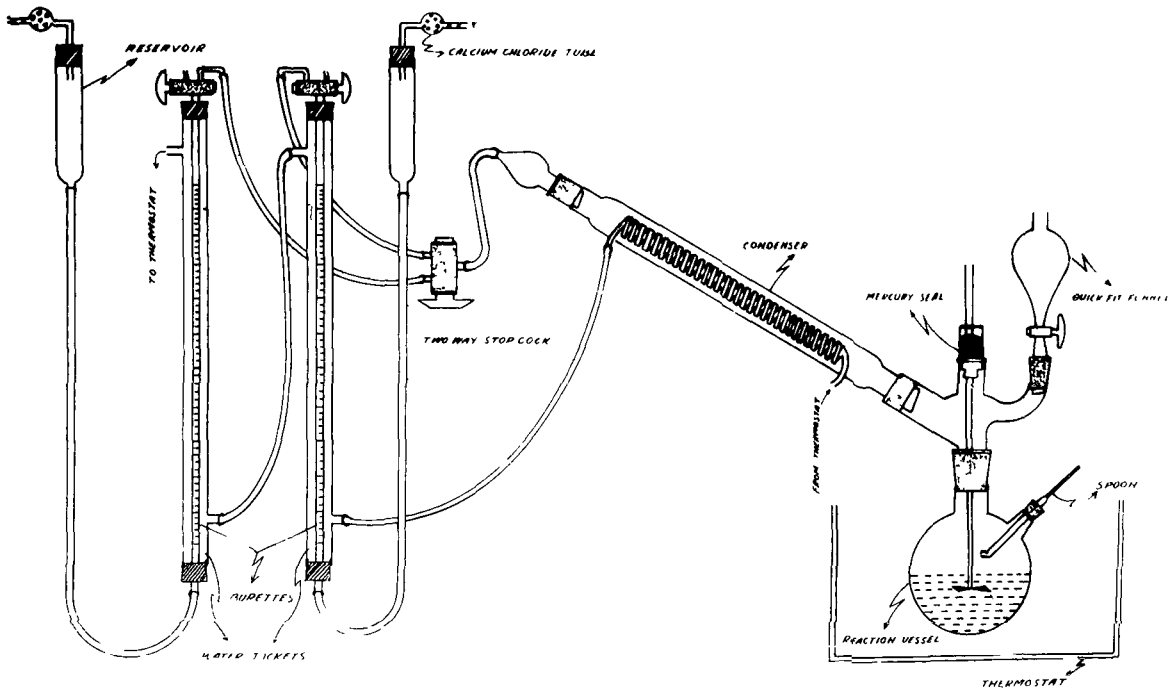
Thiophene Test

Isatin (10 mg) was dissolved in 10 ml of conc. sulphuric acid. To this solution three cc of benzene was added and allowed to stand for a short time. Development of a bluish green colouration in the benzene layer indicates the presence of thiophene.

Chloroform[103]

Commercial chloroform contains ethyl alcohol upto 1%, which is added as a stabiliser. The alcohol was removed by the following procedure:

Chloroform was shaken five times with about half of its volume of water, and distilled. The distillate at 61°C was collected and was kept in dark in sealed bottles to avoid the photochemical formation of phosgene.


RESERVOIR
CALCIUM CHLORIDE TUBE
TO THERMOSTAT
CONDENSER
MERCURY SEAL
QUICK FIT FUNNEL
TWO WAY STOP COCK
FROM THERMOSTAT
SPOON
PIPETTES
REACTION VESSEL
THERMOSTAT

Nitrobenzene[104]

Nitrobenzene was mixed with dilute sulphuric acid and distilled by steam distillation. From the distillate, nitrobenzene was separated; dried with calcium chloride and distilled again and the distillate at 210° was collected and stored in sealed bottles.

DESCRIPTION OF THE APPARATUS

Following is the description of the essential parts of the apparatus shown in the diagram.

Reaction Vessel

It is a hundred ml. quick fit flask fitted with three way quick fit adopter. The reaction vessel was kept immersed in thermostat maintained at constant temperature.

Separating Funnel

One of the side arms of the adopter carried a quick fit separating funnel through which the reactants were introduced.

Water Condenser

The product gases were passed through a condenser (fitted in one side arm of the adopter) through which water at bath temperature was circulated from thermostatic water bath.

Gas Burettes

A double burette assembly was connected with the condenser through a three-way glass-stop-cock. The burettes were jacketed by glass condensers through which water was circulated from the thermostatic bath to keep the gases in thermal equilibrium. The product gases coming out of the condenser were collected in a gas burette over dry glacial acetic acid in which the gases do not dissolve. The reservior of the gas burettes carried anhydrous calcium chloride tube to keep the acid dry.

Mercury seal and Stirrer

A glass rod which passed co-axially through the mercury seal was fitted in an electric motor and was used to stir the reactants.

Before starting the experiment the apparatus was always tested against air leak as follows.

The mercury level in the mercury seal rose up or fell down according as the level of the liquid in the gas burette was raised up or lowered down (with the help of the reservior) and remained in its position.

PREPARATION OF SOLUTIONS

Solutions of the reactants were prepared by volume on the following basis

$$V = \frac{M}{D}$$

where M = molecular weight of the reagent

D = density of the reagent

V = molar volume

A measured volume of the reactant was dissolved in solvent and the volume was made upto one litre to obtain 1M solution. By this way the solution of any desired concentration was prepared.

C A L C U L A T I O N S

The concentration of the reactants at different intervals was calculated as follows:

According to Avagrod's hypothesis, 22,400 ml of a gas at N.T.P. contains its gram molecular weight.

For the reaction

$$R\ COOH + SOCl_2 \longrightarrow R\ COCl + HCl + SO_2$$

it is evident that 2 x 22,400 ml of gas will be evolved from one gram mole of the reactants at N.T.P. In other words thousand ml. of molar solution of the reactants will give 2 x 22,400 ml of the gas at N.T.P. This volume would be equivalent to the volume V^1 of the gas evolved from the complete interaction of 1 mole of the reactants and collected at the bath temperature T^1 and atmospheric pressure P'.

The concentration of the reactants (unreacted) at any time (corresponding to the volume of the gas evolved) can easily be calculated. The following example would illustrate the calculation.

Reaction Mixture

10 ml each 2M R COOH and 2M $SOCl_2$ (in a desired solvent). Total volume of the reaction mixture = 20 ml.

Conditions

Mean atmospheric pressure = 752.0 mm

Reaction bath temperature = 20 $\pm$ 0.1°C

Time (Min.)	5	10	15	20	25	30	35	40	45	50
Total vol. of gas evolved in ml.	45.8	64.7	73.3	80.3	84.2	89.0	92.8	96.0	99.5	104.0

1000 ml of molar solution on complete interaction would give 2 x 22,400 ml at N.T.P. The volume V′ sould be

$$\frac{P'V'}{T'} = \frac{760 \times 44800}{273}$$

$$V' = \frac{T'}{P'} \cdot \left(\frac{760 \times 44800}{273} \right) = \frac{T'}{P'} \cdot 121.$$

$$= 48500 \text{ ml.}$$

Since this volume is evolved from one mole. Therefore 1 ml of the gas would mean the complete chlorination of $\frac{1}{V'}$ or $\frac{P'}{T' \cdot 121}$ mole of the acid. This may be taken as common factor. Therefore, it is possible to calculate the amount of the acid consumed after any interval for which the amount of gas evolved is known. For instance, according to the data given in the above table, 45.8 ml of the gas (mixture) is evolved in 5 minutes. It should be recalled here that had the reaction mixture been 1 litre instead of 20 ml, the volume of the gas evolved would have been 45.5 x 50 ml. And it is this volume which is V′ in the foregoing lines. Therefore,

the amount of the acid consumed per litre in five minutes interval will be $\frac{P'}{121\ T'}$ moles litre $^{-1}$. Thus the unreacted acid will be $(1 - \frac{P'}{121\ T'})$ mole litre^{-1}.

The same treatment was applied with other data and consequently the unreacted acid left at different intervals of time was known. For calculating the concentration of the reactants at any time, it was, however, assumed that they react only as follows:

$$R\ COOH + SOCl_2 \rightleftharpoons R\ COCl + SO_2 + HCl.$$

Integration and isolation methods were employed to determine the total order of the reaction as well as the order with respect to each reactant.

Integration Method

In cases where the reactants were taken in equimolecular proportion, the simple second order equation

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

was found satisfactory. The rate constants were determined from the slopes of time versus concentration inverse plots.

Benzene was used as the solvent for the entire work presented in this chapter unless mentioned otherwise.

Fig No. 1

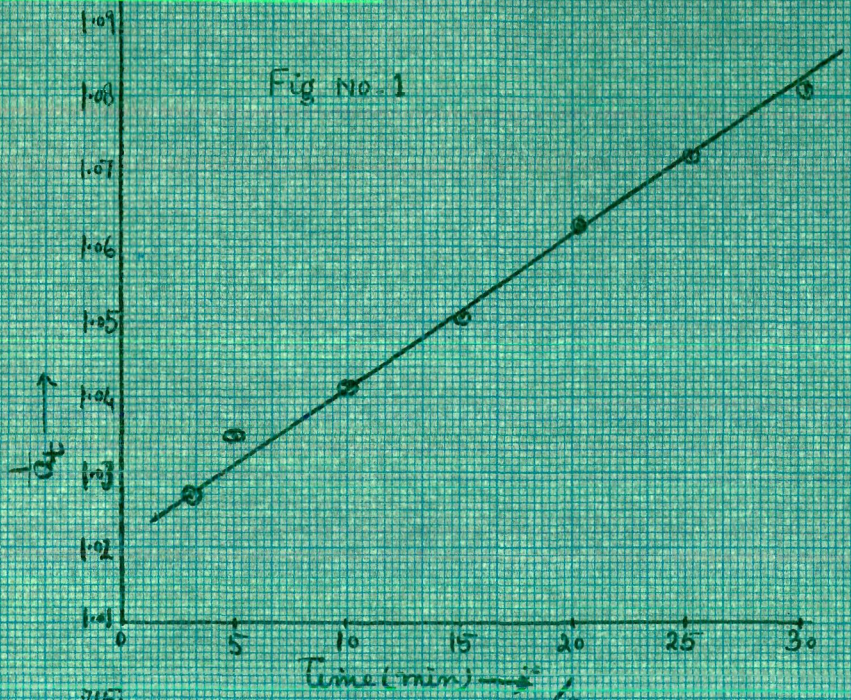


Fig No. 2

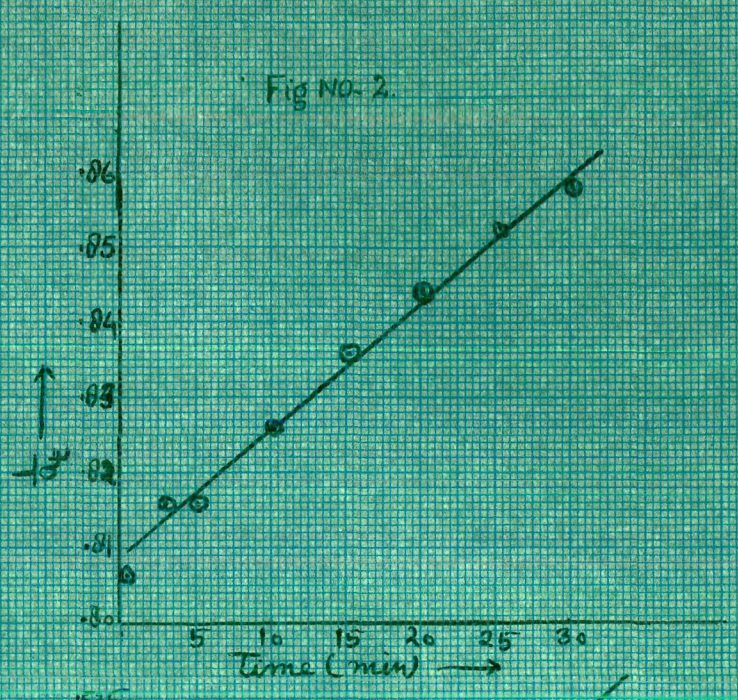


Fig No. 3

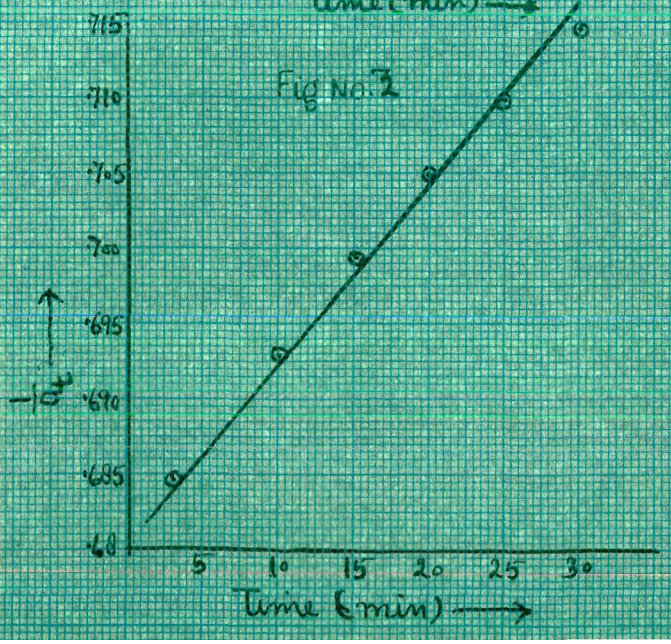
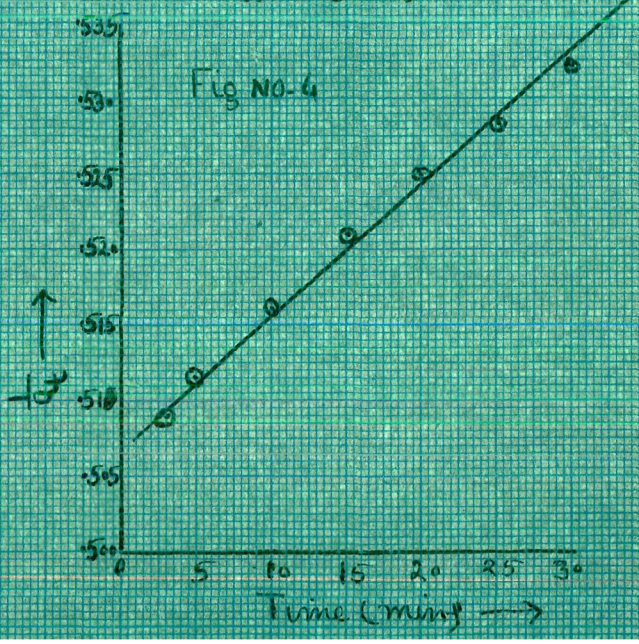


Fig No. 4



Studies with Acetic Acid

Table - 1.

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 752.5 mm.

Reaction mixture : 10 ml 2M CH_3COOH + 10 ml 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
3	27.2 ml	0.9736 mole litre^{-1}
5	34.0 "	0.9664 " "
10	43.7 "	0.9607 " "
15	52.6 "	0.9527 " "
20	60.1 "	0.9405 " "
25	66.7 "	0.9339 " "
30	72.6 "	0.9281 " "

Rate constant = 34.3 x 10^{-6} litre mole^{-1} sec^{-1} (Fig. 1)

Table - 2.

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 752.4 mm.

Reaction mixture: 10 ml. 2.5M CH_3COOH + 10 ml. 2.5M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	9.0 ml	1.2410 mole litre^{-1}
3	37.5 "	1.2138 " "
5	44.2 "	1.2065 " "
10	55.9 "	1.1947 " "
15	64.7 "	1.1870 " "
20	72.5 "	1.1783 " "
25	78.2 "	1.1715 " "
30	83.2 "	1.1676 " "

Rate constant = 28.3 x 10^{-6} litre mole^{-1} sec^{-1} (Fig. 2)

Table - 3.

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 752.4 mm.

Reaction mixture : 10 ml 3M CH_3COOH + 10 ml. 3M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	9.2 ml.	1.491 mole litre^{-1}
3	38.3 "	1.463 " "
10	59.4 "	1.442 " "
15	71.4 "	1.429 " "
20	81.2 "	1.416 " "
25	89.8 "	1.412 " "
30	90.2 "	1.410 " "

Rate constant = 17.5 x 10^{-6} litre mole^{-1}sec^{-1} (Fig. 3)

Table - 4.

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 752.0 mm.

Reaction mixture : 10 ml 4M CH_3COOH + 10 ml 4M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	12.2 ml	1.980 mole litre^{-1}
3	38.8 "	1.9618 " "
5	49.0 "	1.9515 " "
10	68.0 "	1.9327 " "
15	84.0 "	1.9169 " "
20	97.2 "	1.9038 " "
25	109.1 "	1.8920 " "
30	120.4 "	1.8800 " "

Rate constant = 15.0 x 10^{-6} litre mole^{-1}sec^{-1} (Fig. 4.)

Isolation Method

It was pointed out by Harcourt and Esson[105] that if one of the reactants in a bimolecular reaction is present in much larger concentration, the experimental order will be with respect to the reactant at lower concentration (the so called isolated reactant), since the concentration of the reactant that is in larger proportion does not change appreciably during the course of the reaction. Later on this method was generalised by Ostwald[106] for a number of reactants. In the present investigation the order with respect to each reactant was determined by isolating the reactants in turn. In each case, the simple first order equation

$$k = \frac{1}{2.303t} \log \frac{a}{(a-x)}$$

was applicable. The specific rate was determined from the slope of the plot of time versus logarithm of concentration inverse.

The results are as follows:

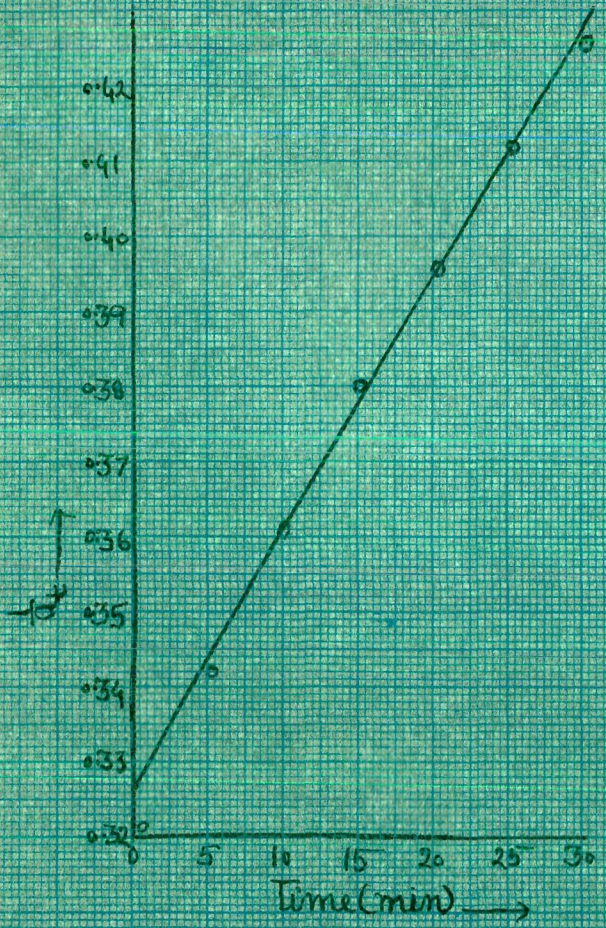


Fig NO.5

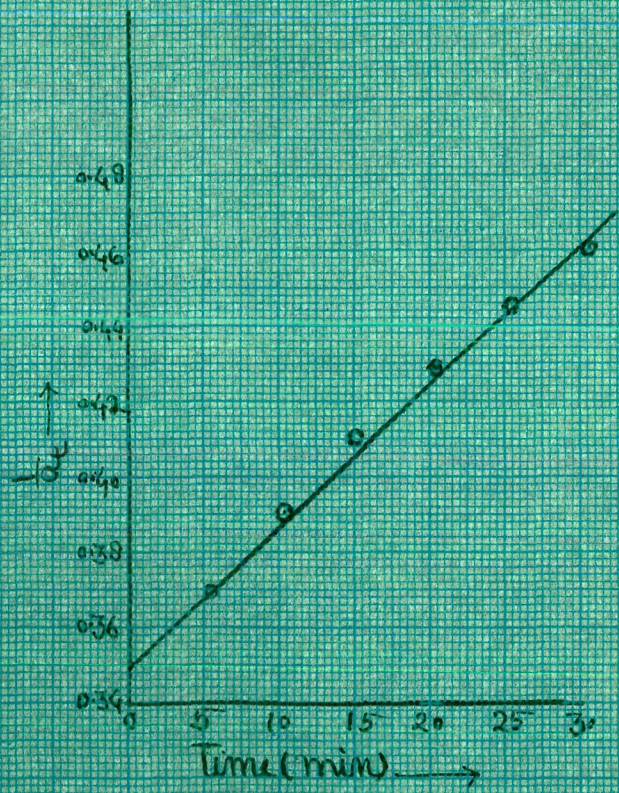


Fig no.6

Table - 5.

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 751.8 mm.

Reaction mixture : 10 ml M CH_3COOH + 10 ml 12M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	12.0 ml	0.4980 mole litre^{-1}
5	44.2 "	0.4545 " "
10	65.0 "	0.4330 " "
15	82.0 "	0.4156 " "
20	96.0 "	0.4011 " "
25	110.0 "	0.3867 " "
30	121.0 "	0.3754 " "

Rate constant = 56.6 x 10^{-6} sec^{-1} (Fig. 5.)

Table - 6.

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 752.0 mm.

Reaction mixture : 10 ml 12M CH_3COOH + 10 ml M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	15.0 ml	0.4800 mole litre^{-1}
5	73.0 "	0.4248 " "
10	100.8 "	0.3962 " "
15	117.8 "	0.3787 " "
20	129.8 "	0.3666 " "
25	140.0 "	0.3558 " "
30	148.2 "	0.3474 " "

Rate constant = 60 x 10^{-6} sec^{-1} (Fig. 6.)

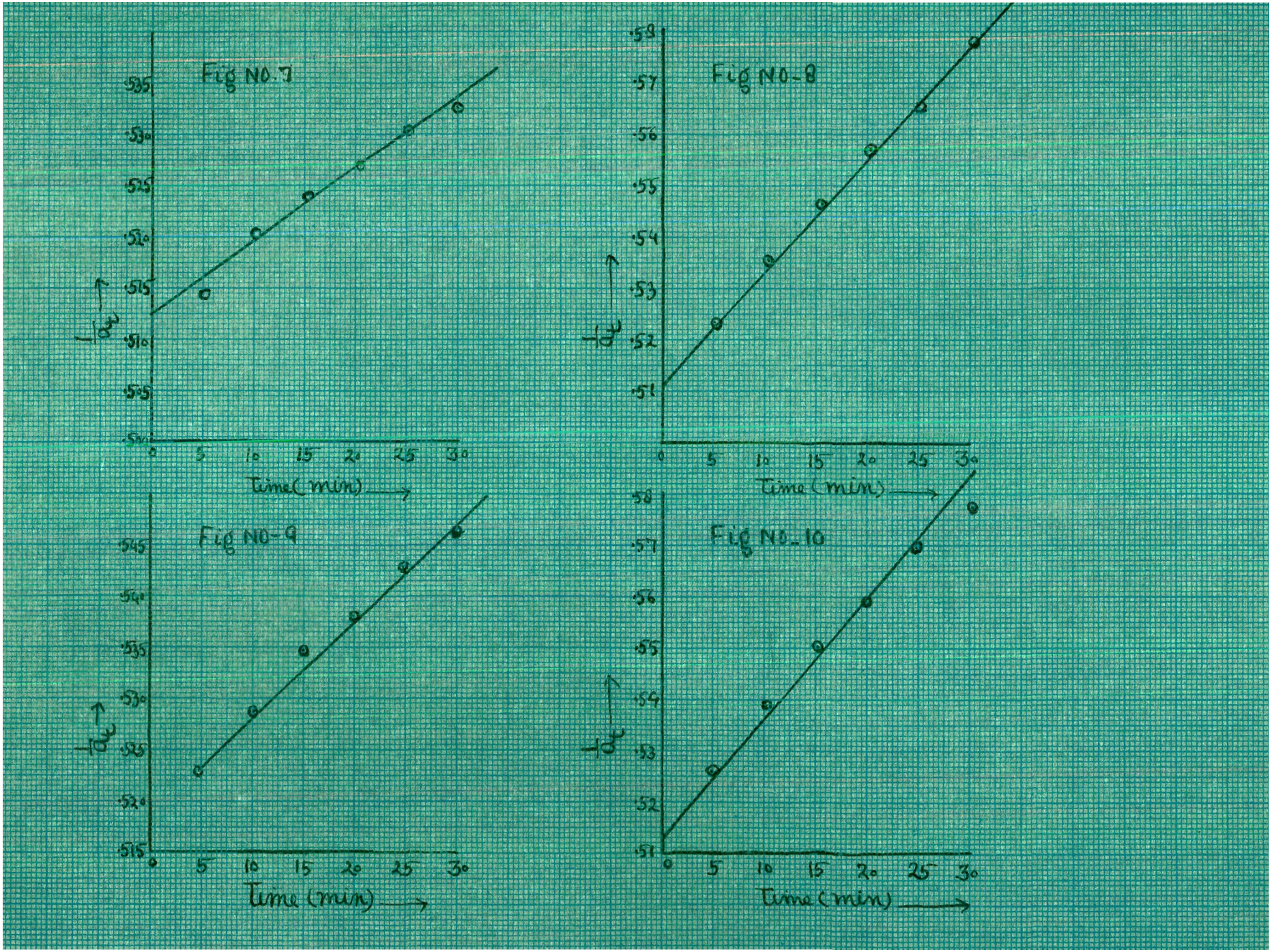


Fig No.7
Fig No.8
Fig No.9
Fig No.10
Time (min)
0
5
10
15
20
25
30

Temperature Coefficient and Activation Energy

The reaction was studied at different temperatures keeping other factors like concentration and solvent (benzene) unchanged.

Table - 7.

Reaction bath temperature = 15 ± 0.1°C
Mean atmospheric pressure = 750.8 mm.
Reaction mixture : 10 ml 4M CH_3COOH + 10 ml 4M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	11.3 ml	1.9887 mole litre^{-1}
5	60.8 "	1.9392 " "
10	77.8 "	1.9222 " "
15	90.3 "	1.9097 " "
20	101.8 "	1.8982 " "
25	111.8 "	1.8882 " "
30	119.3 "	1.8807 " "

Rate constant = 11.66×10^{-6} litre mole^{-1}sec^{-1} (Fig. 7.)

Table - 8.

Reaction bath temperature = 20 ± 0.1°C

Mean atmospheric pressure = 751.0 mm

Reaction mixture : 10 ml 4M CH_3COOH + 10 ml 4M $SoCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	12.2 ml	1.9877 mole litre^{-1}
5	89.5 "	1.9096 " "
10	112.5 "	1.8864 " "
15	129.7 "	1.8690 " "
20	144.7 "	1.8539 " "
25	158.3 "	1.8400 " "
30	170.0 "	1.8280 " "

Rate constant = 15.61 x 10^{-6} litre mole^{-1}sec^{-1} (Fig. 8.)

Table - 9.

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 751.0 mm

Reaction mixture : 10 ml 4M CH_3COOH + 10 ml 4M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	45.0 ml	1.958 mole litre^{-1}
5	109.6 "	1.899 " "
10	151.6 "	1.862 " "
15	179.0 "	1.819 " "
20	202.4 "	1.795 " "
25	222.4 "	1.775 " "
30	238.4 "	1.740 " "

Rate constant = 38.33 x 10^{-6} litre mole^{-1}sec^{-1} (Fig. 9.)

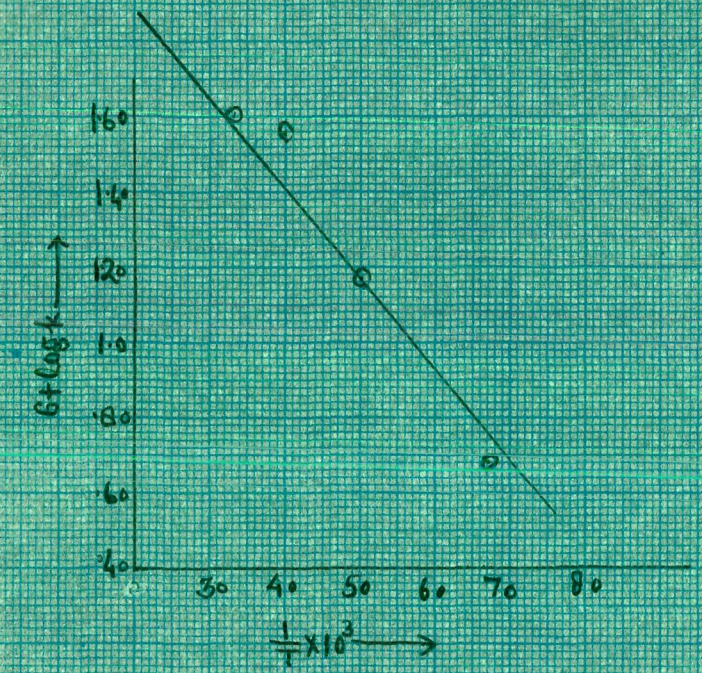


Fig. No. 11

Table - 10.

Reaction bath temperature = 30 ± 0.1°C

Mean atmospheric pressure = 750.8 mm

Reaction mixture : 10 ml 4M CH_3COOH + 10 ml 4M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	45.8 ml	1.958 mole litre^{-1}
5	122.7 "	1.890 " "
10	159.7 "	1.850 " "
15	189.7 "	1.812 " "
20	210.0 "	1.792 " "
25	228.7 "	1.762 " "
30	243.7 "	1.744 " "

Rate constant = 43.6 x 10^{-6} litre mole^{-1}sec^{-1} (Fig. 10.)

Calculation

According to Arrhenius equation

$$\log k = \log A - \frac{E}{2.303RT}$$

where k = specific rate constant

A = frequency factor

R = gas constant

E = Experimental energy of activation

T = Temperature in absolute.

When logarithm of rate constant k was plotted against temperature inverse, a straight line was obtained (see Fig.11). The energy of activation (experimental) as was determined from the slope which was -2.355 x 10^3.

The activation energy, therefore, came out to be 10.7 K Cals mole^{-1}.

Fig No.11
Time (min) →
Fig No.12
Time (min) →
Fig No.13
Time (min) →
Fig No.14
Time (min) →

Influence of Solvents

The kinetics of the reaction was followed in solvents of different dielectric constants. The results are given in the following tables.

Table - 11.

Solvent ——— Chloroform
Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 750.8 mm
Reaction mixture : 10 ml 2M CH_3COOH + 10 ml 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	10.1 ml	0.988 mole litre^{-1}
5	32.0 "	0.968 " "
10	51.8 "	0.948 " "
15	59.6 "	0.940 " "
20	65.0 "	0.935 " "
25	71.4 "	0.929 " "
30	77.0 "	0.923 " "

Rate constant = 31.66×10^{-6} litre mole^{-1}sec^{-1} (Fig. 12.)

Table - 12.

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 751.0 mm

Reaction mixture : 10 ml 3M CH_3COOH + 10 ml 3M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
5	45.0 ml	1.455 mole litre^{-1}
10	65.3 "	1.435 " "
15	83.3 "	1.417 " "
20	96.2 "	1.404 " "
25	108.0 "	1.396 " "
30	118.5 "	1.381 " "

Rate constant = 25 x 10^{-6} litre mole^{-1}sec^{-1} (Fig. 13.)

Table - 13.

Solvent ——— Nitrobenzene

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 751.2 mm

Reaction mixture : 10 ml 2M CH_3COOH + 10 ml 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	15.0 ml	0.994 mole litre^{-1}
1	56.0 "	0.944 " "
5	78.6 "	0.921 " "
10	106.6 "	0.883 " "
15	128.9 "	0.871 " "
20	147.9 "	0.852 " "
25	164.5 "	0.836 " "
30.	178.5 "	0.921 " "

Rate constant = 83.3 x 10^{-6} litre mole^{-1}sec^{-1} (Fig. 14)

Table - 14.

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 751.8 mm

Reaction mixture : 10 ml 3M CH_3COOH + 10 ml 3M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	14.6 ml	1.498 mole litre^{-1}
5	91.3 "	1.409 " "
10	118.3 "	1.381 " "
15	142.0 "	1.358 " "
20	165.0 "	1.335 " "
25	186.5 "	1.314 " "
30	206.8 "	1.290 " "

Rate constant = 79.0 x 10^{-6} litre mole^{-1}sec^{-1}(Fig. 15.)

Table - 15.

Solvent ——— Benzene

Reaction bath temperature = 25 ± 0.1°C

Mean atmospheric pressure = 752.0 mm

Reaction mixture : 10 ml 2M CH_3COOH + 10 ml 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	9.3 ml	0.991 mole litre^{-1}
5	34.0 "	0.966 " "
10	43.7 "	0.961 " "
15	52.6 "	0.952 " "
20	60.1 "	0.940 " "
25	66.7 "	0.933 " "
30	72.6 "	0.928 " "

Rate constant = 34.3 x 10^{-6} litre mole^{-1}sec^{-1}(Fig. 1.)

Table - 16.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 752.8 mm
Reaction mixture : 10 ml 3M CH_3COOH + 10 ml 3M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	10.0 ml	1.490 mole litre^{-1}
3	38.3 "	1.463 " "
10	59.0 "	1.441 " "
15	72.0 "	1.419 " "
20	83.1 "	1.401 " "
25	92.0 "	1.392 " "
30	99.0 "	1.384 " "

Rate constant = 66.6 x 10^{-6} litre mole^{-1}sec^{-1}(Fig. 3.)

Influence of Chain length

To understand the influence of substitution in alkyl group on fatty acid thionyl chloride system, the kinetics was followed likewise with propionic acid in benzene. Propionic acid (A.R.; B.D.H.) was used after distillation in an all glass apparatus. It was kept over anhydrous calcium chloride in a vacuum desiccator.

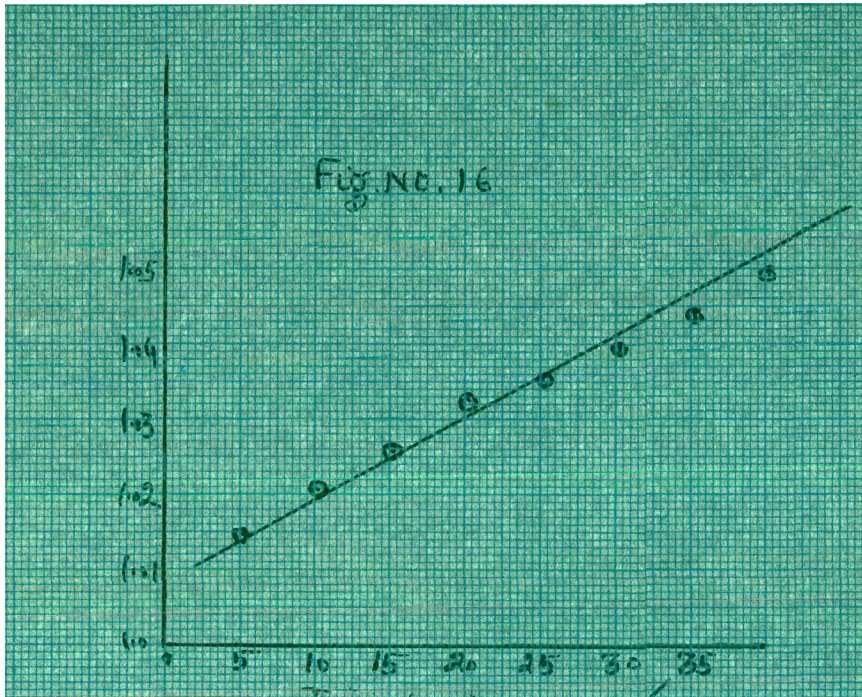


Fig. No. 16

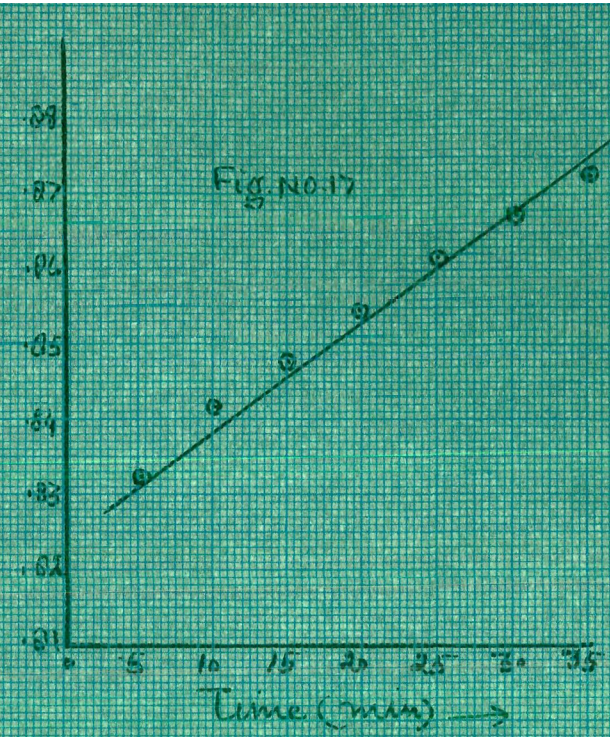


Fig. No. 17

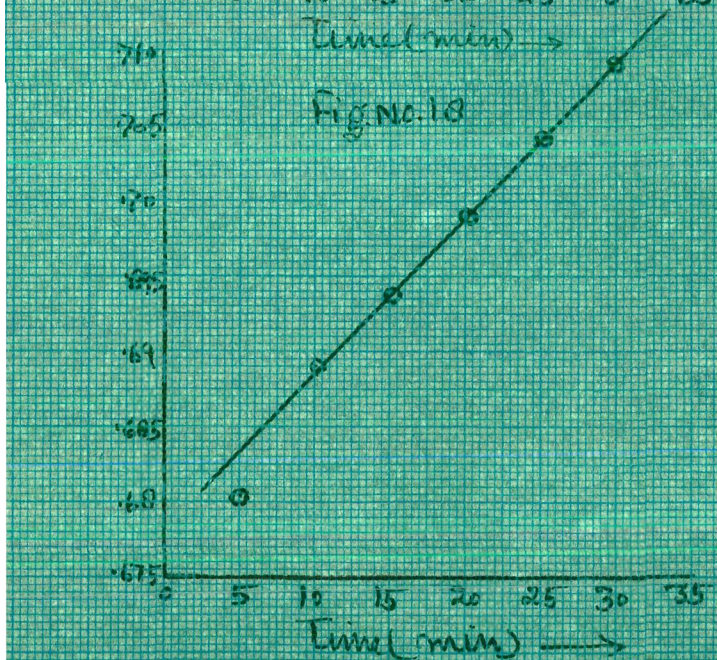


Fig. No. 18

Table - 17.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 751.8 mm
Reaction mixture : 10 ml 2M CH_3CH_2COOH + 10 ml 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	5.6 ml	.991 mole litre^{-1}
5	16.6 "	0.984 " "
10	22.0 "	0.978 " "
15	27.0 "	0.973 " "
20	31.2 "	0.969 " "
25	38.3 "	0.962 " "
35	41.8 "	0.958 " "
40	45.5 "	0.953 " "

Rate constant = 17.5 x 10^{-6} litre mole^{-1} sec^{-1} (Fig. 16)

Table - 18.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 751.8 mm
Reaction mixture: 10 ml 2.5M CH_3CH_2COOH + 10 ml 2.5M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	6.3 ml	1.198 mole litre^{-1}
5	18.0 "	1.192 " "
10	25.0 "	1.175 " "
15	32.0 "	1.168 " "
20	38.0 "	1.162 " "
25	42.5 "	1.157 " "
30	46.7 "	1.153 " "
35	57.7 "	1.149 " "

Rate constant = 15 x 10^{-6} litre mole^{-1} sec^{-1} (Fig. 17).

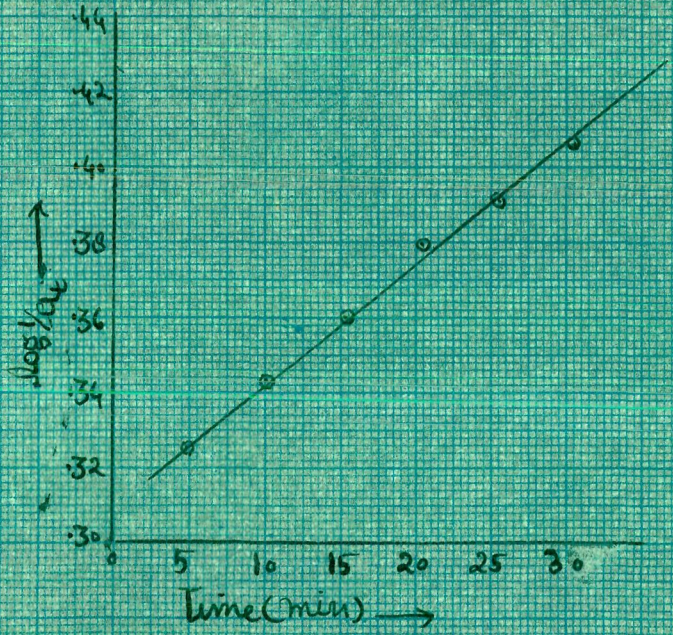


Fig No-19

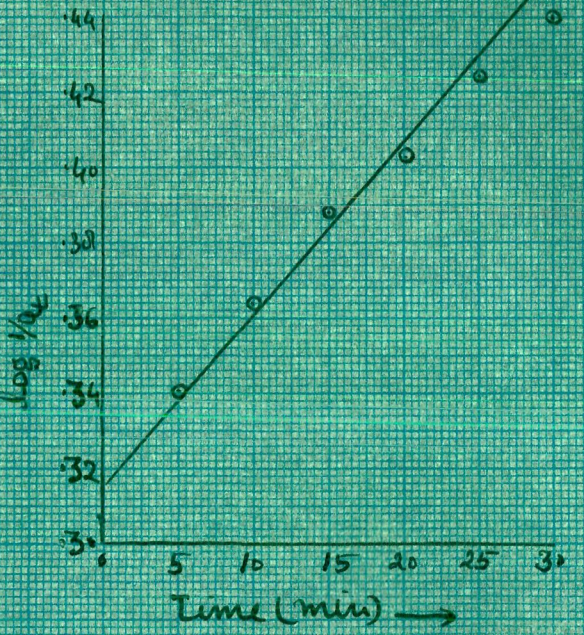


Fig No-20

Studies with Propionic Acid

Table - 19.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 751.8 mm
Reaction mixture : 10 ml 3M CH_3CH_2COOH + 10 ml 3M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	13.2 ml	1.488 mole litre^{-1}
5	40.0 "	1.462 " "
10	52.0 "	1.449 " "
15	62.0 "	1.441 " "
20	71.0 "	1.430 " "
25	79.0 "	1.421 " "
30	87.0 "	1.412 " "
35	94.5 "	1.405 " "

Rate constant = 30 x 10^{-6} litre mole^{-1}sec^{-1}(Fig. 18.)

Isolation Method

Ostwald's method of isolation was employed to determine the order with respect to each reactant by taking them in the ratio of 1:12.

Table - 20.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 751.3 mm
Reaction mixture : 10 ml M CH_3CH_2COOH + 10 ml 12M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	9.2 ml	0.491 mole litre^{-1}
5	30.2 "	0.469 " "
10	50.0 "	0.450 " "
15	68.1 "	0.432 " "
20	84.3 "	0.416 " "
25	98.3 "	0.402 " "
30	110.5 "	0.390 " "

Rate constant = 25.3 x 10^{-6} litre mole^{-1}sec^{-1}(Fig. 19.)

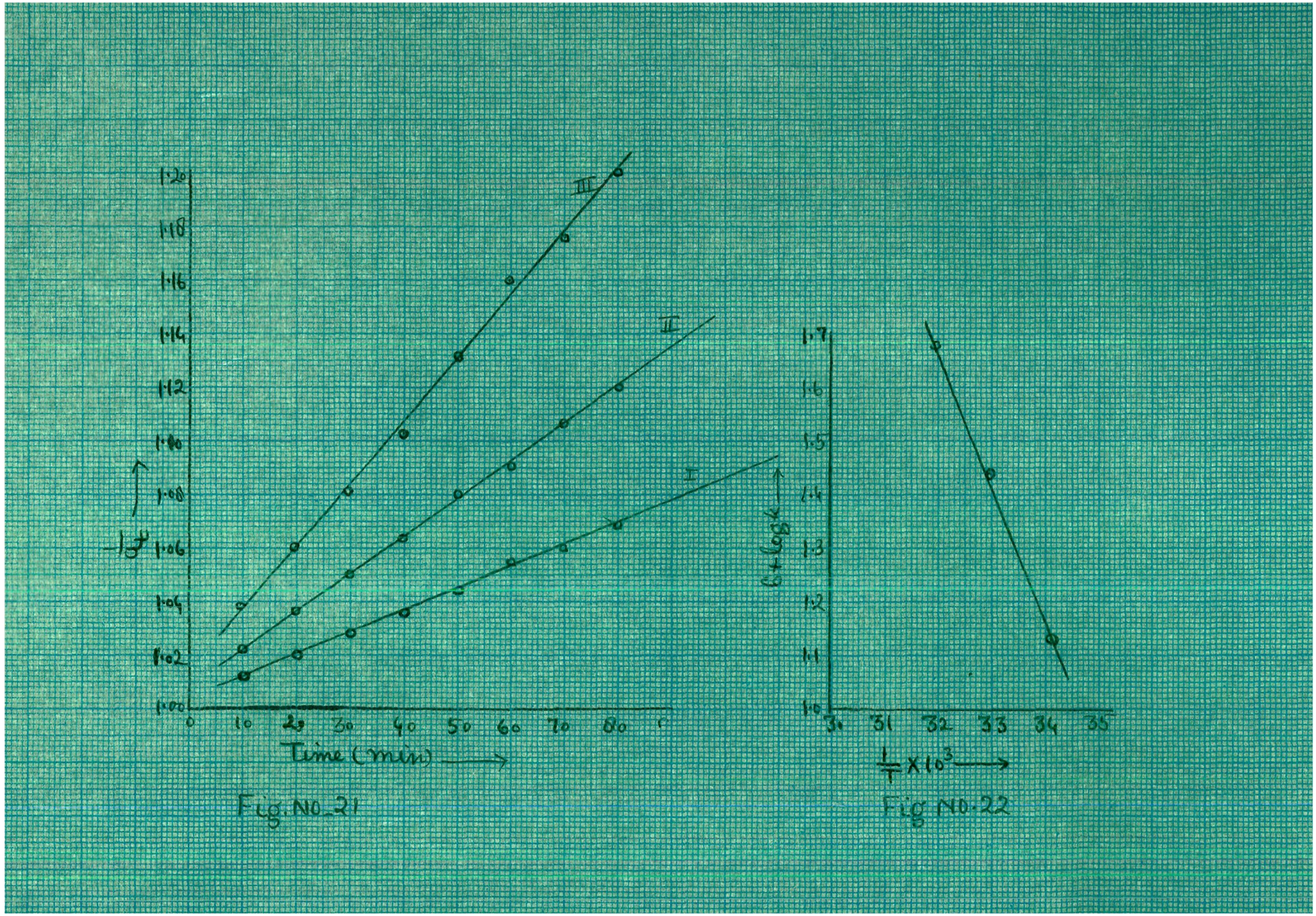


Fig: NO-21

Fig: NO-22

Table - 21.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 751.3 mm
Reaction mixture : 10 ml 2M CH_3CH_2COOH + 10 ml 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	12.3 ml	0.488 mole litre^{-1}
5	46.0 "	0.454 " "
10	70.5 "	0.429 " "
15	92.1 "	0.408 " "
20	110.3 "	0.390 " "
25	123.0 "	0.377 " "
30	133.4 "	0.367 " "

Rate constant = 31.8 x 10^{-6} litre mole^{-1}sec^{-1} (Fig. 20)

Temperature dependence and Activation Energy

Influence of temperature on reaction rate was studied by following the reaction in benzene between 20 and 40°C.

Table - 22.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 743.5 mm
Reaction mixture : 10 ml 2M CH_3CH_2COOH + 10 ml 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	3.2 ml	0.998 mole litre^{-1}
10	12.5 "	0.9874 " "
20	20.0 "	0.9798 " "
30	27.3 "	0.9724 " "
40	35.0 "	0.9646 " "
50	42.6 "	0.9570 " "
60	50.0 "	0.9495 " "
70	57.2 "	0.9422 " "
80	64.0 "	0.9354 " "

Rate constant = 13.43 x 10^{-6} litre mole^{-1}sec^{-1} (Curve 1, Fig. 21).

Table - 23.

Reaction bath temperature = $30 \pm 0.1^{o}C$

Mean atmospheric pressure = 742.7 mm

Reaction mixture : 10 ml 2M CH_3CH_2COOH + 10 ml 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	8.3 ml	0.992 mole : litre^{-1}
10	26.0 "	0.9746 " "
20	38.2 "	0.9627 " "
30	50.2 "	0.9508 " "
40	61.8 "	- " "
50	73.2 "	0.9394 " "
60	84.5 "	0.9172 " "
70	95.6 "	0.9063 " "
80	106.0 "	0.8960 " "

Rate constant = 27.7×10^{-6} litre mole^{-1} sec^{-1}

(Curve II - Fig. 21 .)

Table - 24.

Reaction bath temperature = $40 \pm 0.1^{o}C$

Mean atmospheric pressure = 744.0 mm

Reaction mixture : 10 ml 2M CH_3CH_2COOH + 10 ml 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	13.3 ml	0.998 mole litre^{-1}
10	52.5 "	0.9510 " "
20	75.8 "	0.9300 " "
30	98.0 "	0.9069 " "
40	120.2 "	0.8858 " "
50	132.0 "	0.8746 " "
60	143.8 "	0.8634 " "
70	155.4 "	0.8524 " "
80	176.8 "	0.8320 " "

Rate constant = 48×10^{-6} litre mole^{-1} sec^{-1}

(Curve III - Fig. 21)

Energy of Activation

Activation energy was calculated from the slope of the curve obtained by plotting logarithm of the rate constant against temperature inverse (see fig. 22).

The slope of the line was -2.8×10^3. Hence,

$E = 13.82$ K Cals $mole^{-1}$

Influence of substitution in alkyl radical

To have a better insite in to the mechanism it was considered worthwhile, to study the influence of substitution in alkyl radical on the kinetics. Studies were made with chloro acetic acids to observe the influence of substitution in the methyl radical. The amount of the gas collected at different intervals with different acids is given in the following table. Rate decreases progressively and with trichloro acetic acid it becomes very slow, hence measurements were made after longer intervals.

Mono and trichloro acetic acids (B.D.H.; L.R.) and dichloro acetic acid (B.D.H.; A.R.) were dried by keeping them over anhydrous P_2O_5 in a vacuum desiccator for about twenty four hours. The sharp melting points were indicative of their purity. Their approximate

solutions of approximately required strengths were prepared in benzene by weighing. The solutions were standardized by titrating them against standard NaOH in presence of excess of water (100 ml water for 10 ml solution).

Table - 25.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 750.8 mm
Reaction mixture : 10 ml each 2M acid and 2M $SOCl_2$

Time (Min.)	Volume of gas evolved with different acids			
	Acetic Acid	Chloro Acetic Acid	Dichloro Acetic Acid	Trichloro Acetic Acid
10	43.7 ml	10.5 ml	8.1 ml	-
20	60.1 "	18.0 "	14.2 "	-
30	72.6 "	22.8 "	19.8 "	1.0 ml
40	94.5 "	27.0 "	23.8 "	-
50	110.0 "	31.2 "	27.6 "	-
60	125.0 "	35.0 "	30.0 "	1.9 "
70	138.0 "	38.5 "	32.5 "	-
80	149.0 "	42.2 "	35.2 "	2.5 "

C H A P T E R - II

INFLUENCE OF SUBSTITUTED GROUPS

Several references on the preparation of substituted acetyl chloride are available but no systematic work seems to have been done on the inductive effect with a view to establish the mechanism of formation. Hence a systematic investigation of inductive effect was undertaken to throw light on the kinetics of fatty acid - thionyl chloride reaction. The kinetics of interaction of thionyl chloride with chloro, bromo, iodo, cyano, trimethyl and phenyl acetic acids were followed as before.

E X P E R I M E N T A L

All the substituted acids used for an investigation were (B.D.H.) analytical grade reagents. These acids were first dried over phosphorous pentoxide and then their solutions of approximate strength were prepared by weighing in nitrobenzene.

The solutions were standardised against standard caustic soda as described earlier. Reaction of each acid with thionyl chloride was followed at two different concentrations at 40°C. Though the technique of following the kinetics was essentially the same as described earlier. The following modification was made in the apparatus to avoide the possibility of moisture getting into the reaction vessel during the addition of the acid. Instead of taking the acid solution into separating funnel, it was taken in a spoon as shown in the diagram. The acid was added to thionyl chloride just by rotating the spoon. With this modification all the acid solution was added at-once and the stirrer could be started just after addition without any delay. This modification could easily avoid the zero reading.

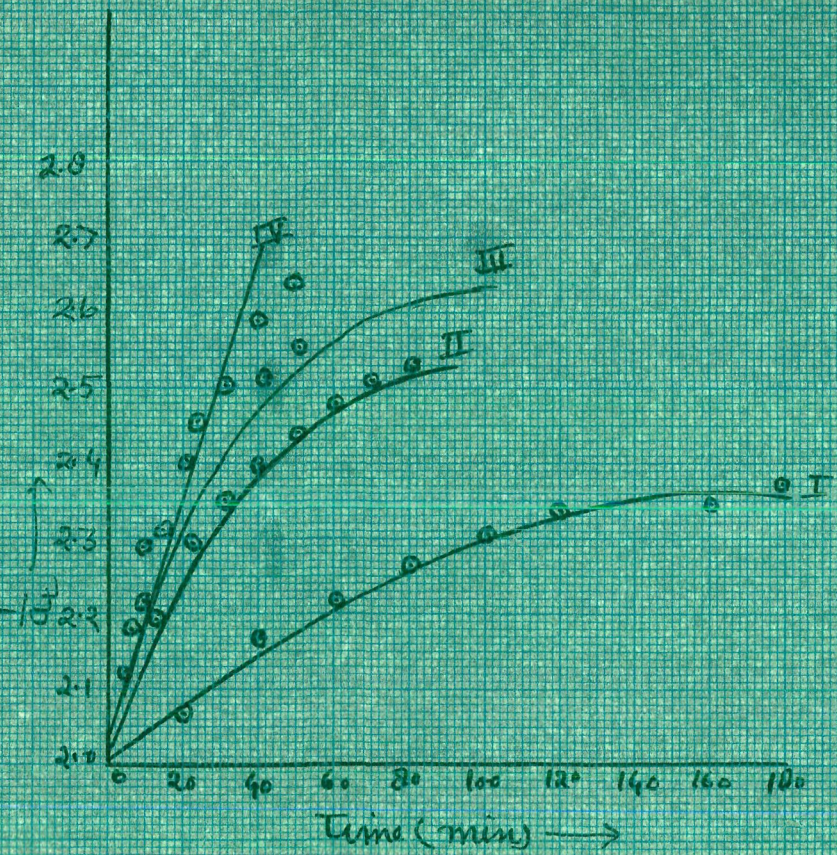

2·8
2·7
2·6
2·5
2·4
2·3
2·2
2·1
2·0
IV
III
II
I
0
20
40
60
80
100
120
140
160
180
Time (min) ⟶

Fig. No. 23

Studies with Chloroacetic acid

Table - 26.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 749.8 mm
Reaction mixture : 10 ml each 2M $ClCH_2COOH$ & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	2.5 ml	0.998 mole litre^{-1}
5	26.5 "	0.973 " "
10	35.7 "	0.964 " "
20	45.3 "	0.955 " "
30	53.0 "	0.947 " "
40	60.0 "	0.939 " "
50	65.2 "	0.935 " "
60	79.5 "	0.919 " "
70	83.3 "	0.917 " "
80	86.0 "	0.914 " "
90	88.5 "	0.911 " "

Table - 27.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 742.0 mm
Reaction mixture : 10 ml each M $ClCH_2COOH$ & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
20	25.4 ml	0.476 mole litre^{-1}
40	44.8 "	0.457 " "
60	56.2 "	0.447 " "
80	65.0 "	0.438 " "
100	71.8 "	0.432 " "
120	75.8 "	0.428 " "
140	78.0 "	0.426 " "
160	80.0 "	0.428 " "
180	82.0 "	0.424 " "
200	83.9 "	0.422 " "

(Curve I Fig. 23)

Studies with Bromoacetic Acid

Table - 28.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 740.0 mm
Reaction mixture : 10 ml each M $BrCH_2COOH$ & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	15.0 ml	0.487 mole litre^{-1}
10	51.0 "	0.452 " "
20	69.5 "	0.434 " "
30	80.0 "	0.424 " "
40	88.0 "	0.416 " "
50	95.0 "	0.410 " "
60	102.2 "	0.403 " "
70	108.4 "	0.397 " "
80	112.4 "	0.393 " "
90	116.2 "	0.389 " "

(Curve II, fig. 23)

Table - 29.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 739.7 mm
Reaction mixture : 10 ml each 2M $BrCH_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	16.8 ml	0.985 mole litre^{-1}
20	110.8 "	0.895 " "
40	136.6 "	0.870 " "
60	153.2 "	0.855 " "
80	168.8 "	0.840 " "
100	182.5 "	0.827 " "
120	207.8 "	0.803 " "
140	215.9 "	0.795 " "
160	228.8 "	0.783 " "
180	238.3 "	0.774 " "
200	244.8 "	0.767 " "

Studies with Iodoacetic Acid

Table - 30.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 749.0 mm
Reaction mixture : 10 ml each 2M ICH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	11.2 ml	0.989 mole litre^{-1}
5	37.0 "	0.963 " "
10	57.5 "	0.943 " "
15	74.3 "	0.926 " "
20	88.3 "	0.912 " "
25	101.1 "	0.899 " "
30	112.8 "	0.887 " "
35	122.3 "	0.878 " "
40	132.0 "	0.868 " "
45	141.0 "	0.859 " "
50	149.8 "	0.851 " "
60	158.4 "	0.842 " "

Table - 31.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 749.0 mm
Reaction mixture : 10 ml each M ICH_2COOH & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	11.2 ml	0.489 mole litre^{-1}
5	45.5 "	0.455 " "
10	66.5 "	0.433 " "
15	80.3 "	0.420 " "
20	88.2 "	0.412 " "
25	94.3 "	0.406 " "
30	98.7 "	0.401 " "
40	105.3 "	0.395 " "
50	110.0 "	0.389 " "
70	115.8 "	0.384 " "
80	118.2 "	0.382 " "
90	120.0 "	0.380 " "
100	121.4 "	0.379 " "

(Curve III, fig. 23)

Studies with Phenyl Acetic Acid

Table - 32.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 752.0 mm
Reaction mixture: 10 ml each 2M $PhCH_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	11.2 ml	0.991 mole litre^{-1}
5	83.0 "	0.921 " "
10	141.0 "	0.865 " "
15	185.5 "	0.822 " "
20	218.0 "	0.791 " "
25	241.0 "	0.769 " "
30	261.5 "	0.749 " "
35	276.5 "	0.735 " "
40	289.8 "	0.722 " "
45	298.8 "	0.712 " "
50	302.8 "	0.709 " "
55	305.8 "	0.706 " "
60	309.0 "	0.703 " "
65	311.8 "	0.701 " "

Table - 33.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 752.0 mm
Reaction mixture: 10 ml each M $PhCH_2COOH$ & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	8.6 ml	0.492 mole litre^{-1}
5	30.0 "	0.471 " "
10	51.5 "	0.449 " "
15	68.8 "	0.432 " "
20	82.5 "	0.418 " "
25	94.5 "	0.406 " "
30	102.0 "	0.399 " "
35	109.5 "	0.392 " "
40	115.3 "	0.386 " "
50	123.3 "	0.378 " "

(Curve IV, fig. 23)

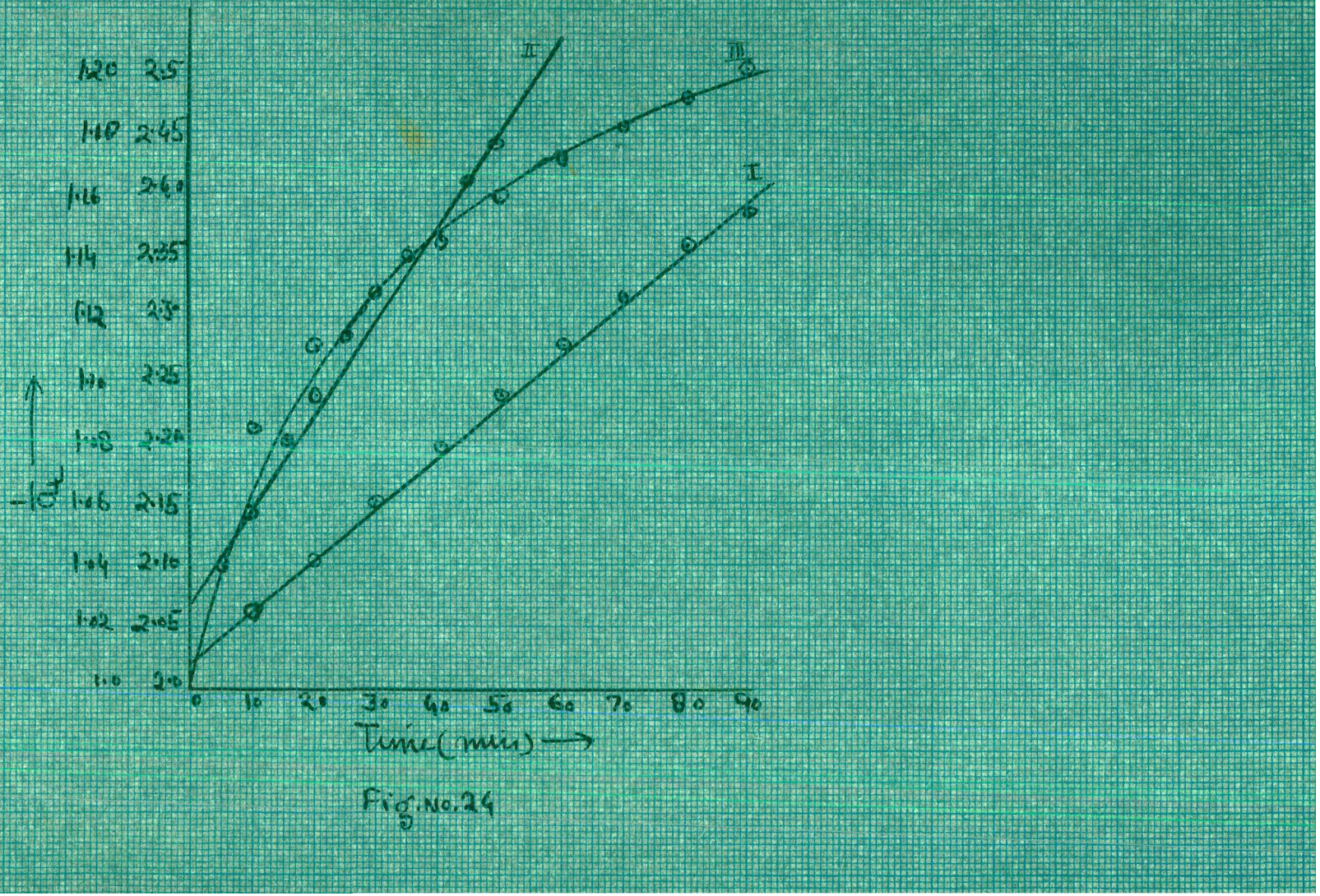

1·20 2·5
1·18 2·45
1·16 2·40
1·14 2·35
1·12 2·30
1·10 2·25
1·08 2·20
1·06 2·15
1·04 2·10
1·02 2·05
1·0 2·0
$-\log\frac{a}{a-x}$
0 10 20 30 40 50 60 70 80 90
Time (min) ⟶
I
II
III

Fig. No. 24

Studies with Trimethylacetic acid

Table - 34.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 749.0 mm
Reaction mixture : 10 ml each 2M $(CH_3)_3CCOOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	10.2 Ml	0.980 mole litre^{-1}
5	37.0 "	0.963 " "
10	57.5 "	0.943 " "
15	74.3 "	0.926 " "
20	88.3 "	0.912 " "
25	102.0 "	0.898 " "
30	113.0 "	0.887 " "
35	122.8 "	0.877 " "
40	132.3 "	0.868 " "
45	141.5 "	0.859 " "
50	150.0 "	0.850 " "
60	159.3 "	0.841 " "

(Curve I, fig. 24).

Table - 35.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 749.0 mm
Reaction mixture: 10 ml each M$(CH_3)_3$-C.COOH & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	6.0 ml	0.495 mole litre^{-1}
5	14.8 "	0.485 " "
10	23.5 "	0.477 " "
20	36.0 "	0.464 " "
30	44.4 "	0.456 " "
40	51.4 "	0.449 " "
50	58.0 "	0.442 " "
60	64.3 "	0.436 " "
70	70.0 "	0.430 " "
80	75.5 "	0.424 " "
90	80.0 "	0.420 " "

(Curve II, fig. 24)

Studies with Cyano acetic acid

Table - 36.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 745.3 mm
Reaction mixture: 10 ml each M $CNCH_2COOH$ & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants		
1	8.2 ml	0.493	mole	$litre^{-1}$
10	53.6 "	0.452	"	"
20	69.0 "	0.439	"	"
30	78.6 "	0.429	"	"
40	86.0 "	0.423	"	"
50	93.6 "	0.416	"	"
60	98.8 "	0.411	"	"
70	103.0 "	0.407	"	"
80	107.0 "	0.404	"	"
90	110.5 "	0.400	"	"
100	113.6 "	0.398	"	"

(Curve III, fig. 24)

For all the acids, plots were made for time versus concentration inverse. But the data for non-excent for trimethylacetic acid were found to give a straight line.

C H A P T E R - III

INFLUENCE OF CHAIN LENGTH

Although acylchlorides of fatty acids of lower as well as higher members have been prepared by the action of thionyl chloride on the respective acid. No reference is available on the relative ease of preparation. The only relevent reference is that of Gerrard. He too has measured the rate for two or three acids.

The influence of chain length on fatty acids - thionyl chloride reaction was undertaken with a view to locate the exact site at which thionyl chloride attacks. The kinetics of interaction with acetic, propionic, bytyric, valeric and caproic acids were made in nitrobenzene. The other higher acid could not be studied in nitrobenzene due to the poor solubility. Hence xylene was employed for capric, lauric, myristic, palmitic, and steric acids. But in xylene too, solutions stronger than 0.5M could not be prepared in some cases due to poor solubility. The reaction of 0.5M acid with 0.5M thionyl chloride was too slow to follow the kinetics. Hence 0.5M solution of each acid was mixed with equal volume of 5M thionyl chloride and the kinetics was followed under identical conditions.

E X P E R I M E N T A L

The reactants and the solvent were purified and dried before use. Acetic and propionic acids were purified as before. n-Bytyric acid (E. Merck) valeric acid (Fluka, L.R.) and caproic acid (B.D.H.L.R.) were used after purification. Nitrobenzene was purified as described earlier. The activation energy for each acid was calculated from the slope of log K versus $\frac{I}{T}$ curves as described in Chapter I.

Purification of Palmitic acid[107]

Palmitic acid was recrystallised five times in 95% ethyl alcohol and then ten times in pure benzene. The product had a sharp melting point 62.6°C.

Purification of Stearic Acid[108]

The acid was recrystallised seven times from 95% alcohol. This after three crystallisations from benzene had constant melting point 69.4°C.

Lauric and myristic acids were also purified in the similar manner. Sharp melting points were taken as the criteria of purity.

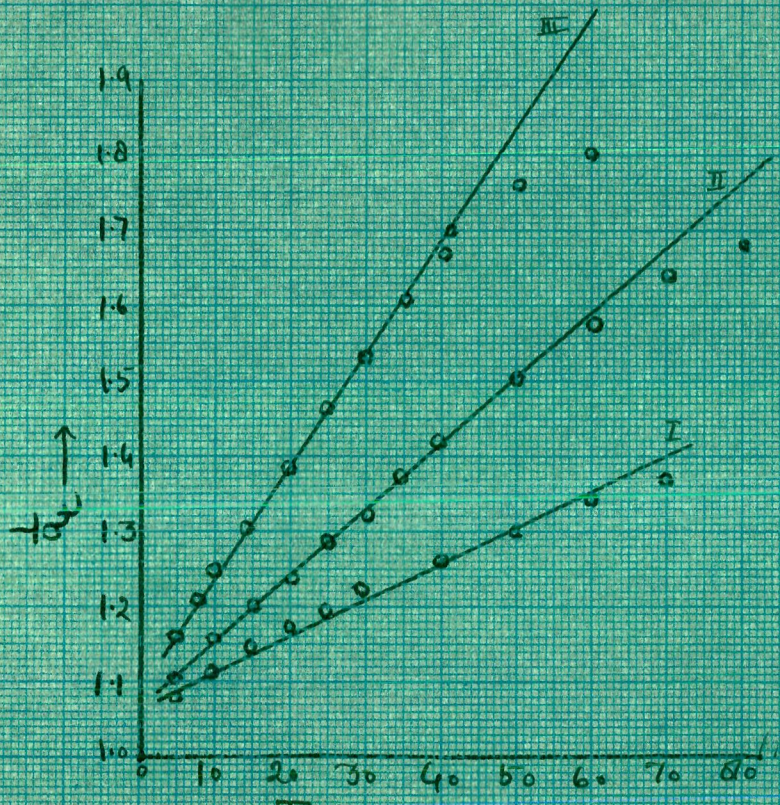


Fig No 25

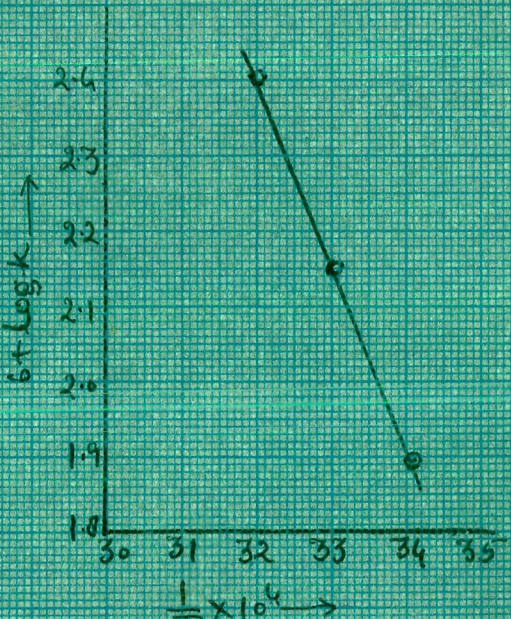


Fig No. 26

Capric Acid

The acid was distilled in all glass assembly. The distillate at 268.7°C was collected and allowed to cool. A white crystalline solid was obtained which melted just at 31.3°C.

Studies with Acetic Acid

Table - 37.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 746.0 mm
Reaction mixture : 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	1.0 ml	1.000 mole litre^{-1}
5	64.0 "	0.936 " "
10	92.2 "	0.906 " "
15	123.4 "	0.877 " "
20	145.4 "	0.855 " "
25	165.2 "	0.835 " "
30	181.2 "	0.819 " "
40	208.2 "	0.792 " "
50	230.2 "	0.770 " "
60	250.0 "	0.749 " "
70	262.0 "	0.738 " "

Rate constant = 79 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve I, fig. 25)

Table - 38.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 744.0 mm
Reaction mixture : 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	1.0 ml	1.000 mole : litre^{-1}
5	97.8 "	0.909 " "
10	144.8 "	0.869 " "
15	174.0 "	0.833 " "
20	194.6 "	0.813 " "
25	227.0 "	0.782 " "
30	252.0 "	0.758 " "
35	281.0 "	0.730 " "
40	308.0 "	0.704 " "
50	346.8 "	0.667 " "
60	378.0 "	0.637 " "
70	402.0 "	0.614 " "
80	418.0 "	0.599 " "

Rate constant = 149 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 25)

Table - 39.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 742.6 mm
Reaction mixture : 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.0 mole : litre^{-1}
5	145.5 "	0.869 " "
10	222.2 "	0.800 " "
15	266.6 "	0.760 " "
20	312.2 "	0.719 " "
25	350.6 "	0.685 " "
30	405.4 "	0.635 " "
35	416.6 "	0.625 " "
40	444.0 "	0.600 " "
50	480.0 "	0.568 " "
60	493.0 "	0.556 " "

Rate constant = 25 x 10^{-5} litre mole^{-1}sec^{-1}
(Curve III, fig. 25)

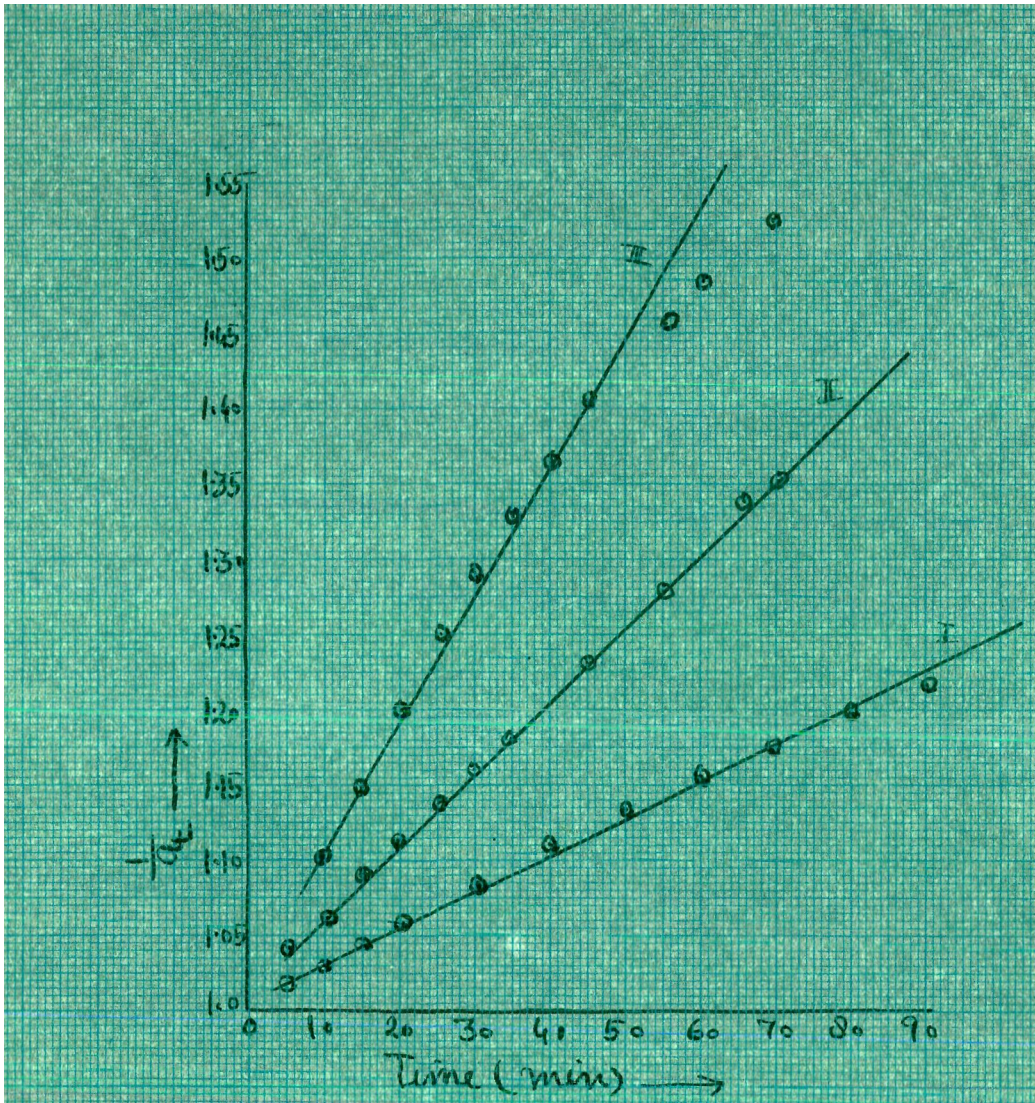


Fig NO 27

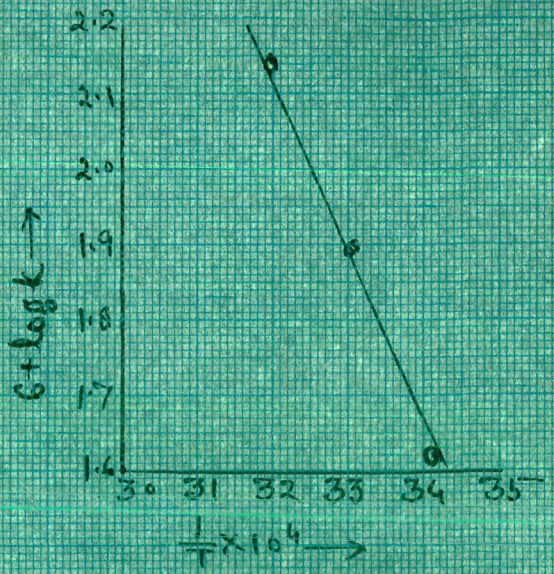


Fig NO 28

The activation energy was calculated by multiplying the slope of log K versus $\frac{1}{T}$ plot (vide fig. 26) by 2.303R. The activation parameters were evaluated at 303°K. The following are the results.

$E = 10.99$ K Cals mole^{-1}

$\Delta E^{\ddagger} = 10.38$ Kcals mole^{-1}

$\Delta F^{\ddagger} = 23.11$ K cals mole^{-1}

$\Delta S^{\ddagger} = -40.0$ eu.

$A = 2 \times 10^{5}$ sec^{-1}

Studies with Propionic Acid

Studies with propionic acid were carried out in the same solvent. The following are the results.

Table - 40.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 733.7 mm
Reaction mixture : 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
5	18.4 "	0.981 " "
10	32.6 "	0.967 " "
15	46.0 "	0.954 " "
20	57.5 "	0.942 " "
30	79.8 "	0.920 " "
40	100.5 "	0.899 " "
50	117.8 "	0.882 " "
60	134.7 "	0.865 " "
70	149.8 "	0.850 " "
80	163.9 "	0.836 " "
90	175.9 "	0.824 " "
100	187.5 "	0.812 " "

Rate constant = 41.7×10^{-6} litre mole^{-1} sec^{-1} (Curve I, fig.27)

Table - 41.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 733.7 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
5	38.0 "	0.964 " "
10	65.5 "	0.940 " "
15	91.0 "	0.918 " "
20	114.2 "	0.892 " "
25	135.0 "	0.872 " "
30	155.5 "	0.852 " "
35	172.4 "	0.836 " "
45	203.3 "	0.807 " "
55	229.0 "	0.782 " "
65	252.0 "	0.761 " "

Rate constant = 79.3 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 27)

Table - 42.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 707.8 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	104.3 "	0.906 " "
15	143.6 "	0.868 " "
20	187.3 "	0.831 " "
25	223.8 "	0.799 " "
30	251.3 "	0.774 " "
35	277.0 "	0.751 " "
40	298.8 "	0.731 " "
45	319.6 "	0.712 " "
55	349.0 "	0.686 " "
60	361.8 "	0.674 " "
70	369.4 "	0.667 " "

Rate constant = 13.9 x 10^{-5} litre mole^{-1} sec^{-1}
(Curve III, fig. 27)

The activation energy was calculated from the slope of figure 28 and the activation parameters were evaluated at 303°K. The following are the values:

$E = 11.22$ K cals $mole^{-1}$

$\Delta E^{\neq} = 10.61$ K cals $mole^{-1}$

$\Delta F^{\neq} = 23.36$ K cals $mole^{-1}$

$\Delta S^{\neq} = 42.0$ e.u.

$A = 3.98 \times 10^{4}$ sec^{-1}

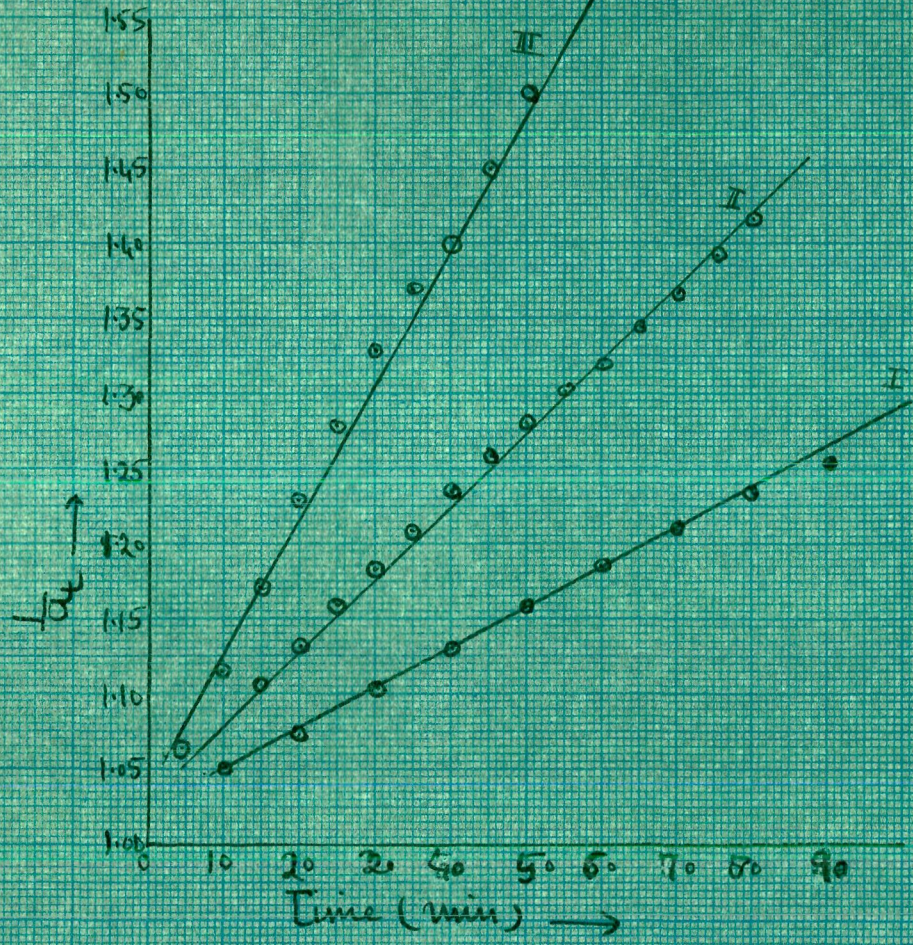


Fig. No. 29

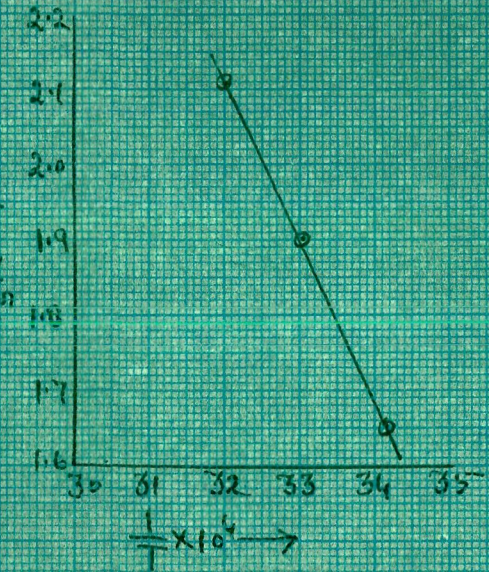


Fig. No. 30

Studies with Butyric Acid

Table - 43.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 743.6 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	37.9	"	0.962	"	"
20	68.2	"	0.932	"	"
30	94.1	"	0.906	"	"
40	115.9	"	0.884	"	"
50	137.3	"	0.863	"	"
60	157.0	"	0.843	"	"
70	174.3	"	0.826	"	"
80	190.0	"	0.810	"	"
90	203.0	"	0.797	"	"

Rate constant = 45 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 29)

Table - 44.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 740.4 mm
Reaction mixture : 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	69.0	"	0.933	"	"
15	94.5	"	0.907	"	"
20	118.3	"	0.884	"	"
25	140.0	"	0.863	"	"
30	160.5	"	0.843	"	"
35	178.3	"	0.826	"	"
40	194.8	"	0.809	"	"
45	209.5	"	0.795	"	"
50	223.5	"	0.781	"	"
55	235.0	"	0.770	"	"
60	246.7	"	0.758	"	"

Rate constant = 80.3 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 29)

Table - 45.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 743.0 mm
Reaction mixture : 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 moles litre^{-1}
5	62.2 "	0.941 " "
10	109.2 "	0.896 " "
15	156.6 "	0.852 " "
20	195.6 "	0.814 " "
25	230.0 "	0.782 " "
30	260.0 "	0.753 " "
35	285.5 "	0.730 " "
40	307.2 "	0.718 " "
45	326.2 "	0.690 " "
50	341.7 "	0.675 " "
65	367.5 "	0.651 " "

Rate constant = 14.88 x 10^{-5} litre mole^{-1}sec^{-1}
(Curve III, fig. 29)

The energy of activation was calculated from the slope of fig. 30. The activation parameters were calculated at 303K. The following are the results

E = 11.45 K cals mole^{-1}

$\Delta E^{\ddagger}$ = 10.84 K cals mole^{-1}

$\Delta F^{\ddagger}$ = 23.4 K cals mole^{-1}

$\Delta S^{\ddagger}$ = -41.4 e.u.

A = 1.4 x 10^5 sec^{-1}

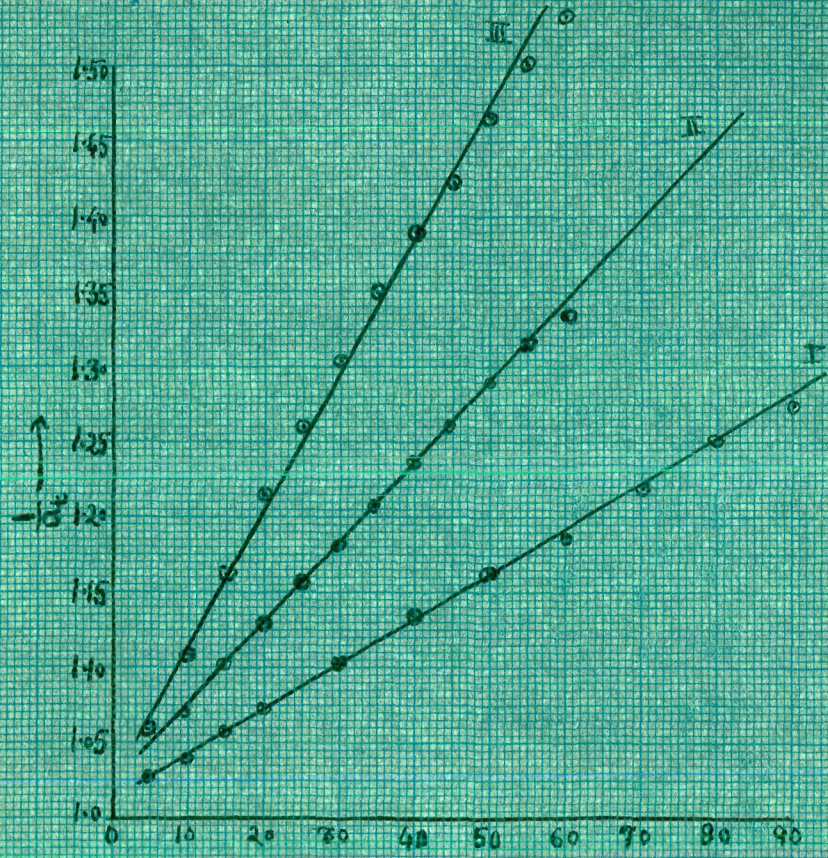


Fig. NO. 31

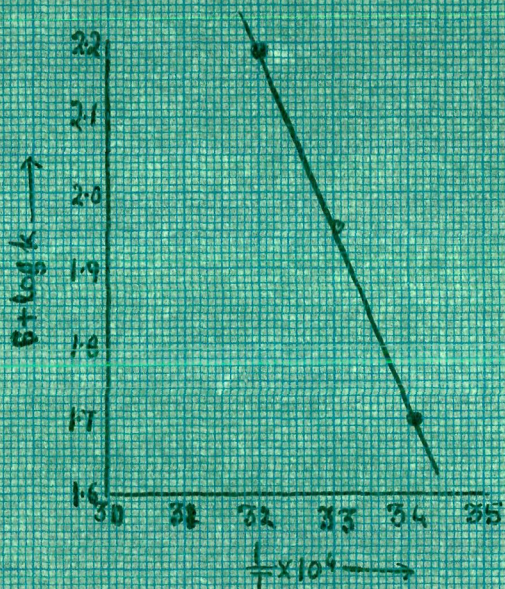


Fig. NO. 32

Studies with Valeric Acid

Studies in Nitrogen

Table - 46.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 741.6 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	$litre^{-1}$
5	23.0	"	0.977	"	"
10	39.7	"	0.960	"	"
15	53.7	"	0.946	"	"
20	68.7	"	0.931	"	"
30	95.8	"	0.904	"	"
40	118.5	"	0.881	"	"
50	140.5	"	0.859	"	"
60	157.3	"	0.843	"	"
70	174.6	"	0.826	"	"
80	188.0	"	0.812	"	"
90	201.0	"	0.799	"	"

Rate constant = 50 x 10^{-6} litre $mole^{-1}sec^{-1}$
(Curve I, fig. 31)

Table - 47.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 741.0 mm
Reaction mixture : 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	$litre^{-1}$
1	16.9	"	0.994	"	"
10	71.0	"	0.932	"	"
15	96.2	"	0.906	"	"
20	118.7	"	0.884	"	"
25	139.2	"	0.864	"	"
30	158.3	"	0.845	"	"
35	175.3	"	0.828	"	"
40	190.2	"	0.814	"	"
45	203.9	"	0.800	"	"
50	216.3	"	0.788	"	"
55	227.5	"	0.777	"	"
60	238.0	"	0.767	"	"

Rate constant = 90.3 x 10^{-6} litre $mole^{-1}sec^{-1}$
(Curve II, fig. 31)

Table - 48.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 740.3 mm
Reaction mixture : 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2m $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0.0	ml	1.00	mole	litre^{-1}
1	23.0	"	0.972	"	"
5	58.3	"	0.945	"	"
10	104.3	"	0.902	"	"
15	148.3	"	0.859	"	"
20	188.3	"	0.821	"	"
25	218.3	"	0.793	"	"
30	246.8	"	0.766	"	"
35	274.8	"	0.739	"	"
40	295.0	"	0.720	"	"
45	312.0	"	0.704	"	"
50	324.0	"	0.689	"	"
55	342.7	"	0.674	"	"
60	355.5	"	0.662	"	"

Rate constant = 15.5 x 10^{-5} litre mole^{-1}sec^{-1}
(Curve III, fig. 31)

The activation energy was determined from the slope of figure 32 and the activation parameters were calculated as before. The results are:

E = 11.22 K cals mole^{-1}

$\Delta E^{\ddagger}$ = 10.61 K cals mole^{-1}

$\Delta F^{\ddagger}$ = 23.4 K cals mole^{-1}

$\Delta S^{\ddagger}$ = - 42.2 e.u.

A = 10 x 10^4 sec^{-1}

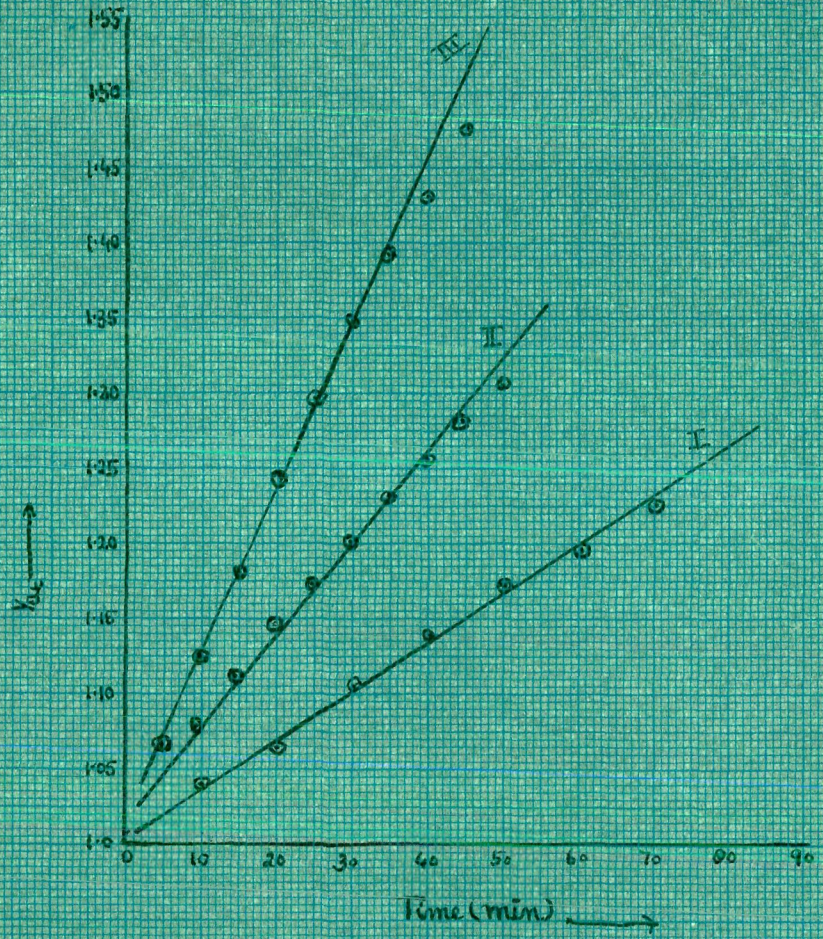


Fig No 33

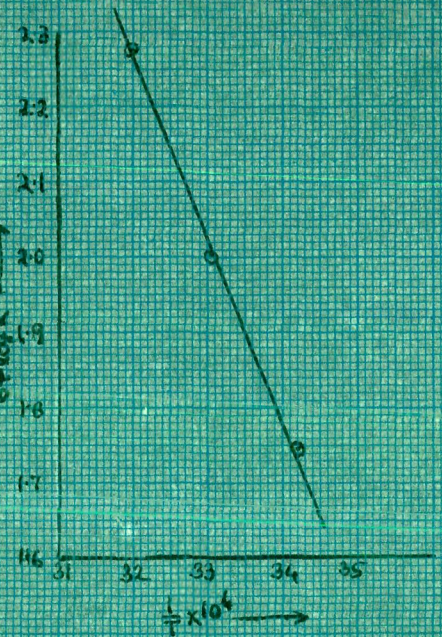


Fig No. 34

Studies with n-caproic Acid

Studies in Nitrobenzene

Table - 49.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 737.6 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_4COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.0	mole	litre^{-1}
10	39.0	"	0.960	"	"
20	70.0	"	0.930	"	"
30	97.8	"	0.902	"	"
40	121.8	"	0.874	"	"
50	144.0	"	0.856	"	"
60	162.8	"	0.837	"	"
70	182.8	"	0.818	"	"

Rate constant = 55.5 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 33)

Table - 50.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 743.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_4COOH$ & 2M $SOCl_2$

Time (Min.)	Voll of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	73.0	"	0.928	"	"
15	101.1	"	0.901	"	"
20	126.9	"	0.898	"	"
25	150.3	"	0.853	"	"
30	171.3	"	0.832	"	"
35	191.3	"	0.813	"	"
40	207.3	"	0.797	"	"
45	222.3	"	0.782	"	"
50	233.0	"	0.772	"	"

Rate constant = 101 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 33)

Table - 51.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 742.8 mm
Reaction mixture = 10 ml each 2M $CH_3(CH_2)_4COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	moles litre^{-1}	
5	66.6	"	0.937	"	"
10	116.6	"	0.889	"	"
15	162.8	"	0.845	"	"
20	204.8	"	0.805	"	"
25	240.5	"	0.772	"	"
30	271.5	"	0.742	"	"
35	296.3	"	0.719	"	"
40	317.4	"	0.699	"	"
45	336.4	"	0.680	"	"
50	351.6	"	0.666	"	"
55	365.6	"	0.653	"	"
60	377.4	"	0.641	"	"

Rate constant = 18.9 x 10^{-5} litre mole^{-1}sec^{-1}
(Curve III, fig. 33)

The activation energy was determined from the slope of figure 34 and the activation parameters were calculated as before. The results are:

E = 11.0 K cals mole^{-1}

$\Delta E^{\ddagger}$ = 10.38 K cals mole^{-1}

$\Delta F^{\ddagger}$ = 23.32 K cals mole^{-1}

$\Delta S^{\ddagger}$ = -42.7 e.u.

A = 7.58 x 10^4sec^{-1}

Studies with higher acids in Xylene

Table - 52.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 743.2 mm
Reaction mixture: 10 ml each 0.5M acid & 5M $SOCl_2$

Time (Min.)	Vol. of gas evolved for different acids				
	n-capric acid	Lauric acid	Myristic acid	Palmitic acid	Stearic acid
0	0 ml	0 ml	0 ml	0 ml	0 ml
10	22.0 "	16.9 "	16.8 "	17.0 "	15.0 "
20	30.2 "	26.5 "	26.0 "	28.0 "	27.0 "
30	36.3 "	34.6 "	33.0 "	36.0 "	32.5 "
40	43.6 "	40.5 "	39.4 "	41.0 "	38.9 "
50	47.8 "	46.7 "	46.0 "	47.0 "	46.0 "
60	53.8 "	52.0 "	53.2 "	54.2 "	49.6 "
70	57.6 "	56.9 "	59.9 "	63.0 "	62.2 "
80	62.3 "	61.2 "	65.8 "	67.2 "	66.3 "
90	66.2 "	65.0 "	68.0 "	69.8 "	68.6 "
100	70.2 "	69.3 "	72.8 "	73.2 "	72.7 "
110	73.0 "	71.6 "	77.4 "	80.0 "	75.8 "
120	82.8 "	81.6 "	82.0 "	84.2 "	82.9 "

C H A P T E R - IV

STUDIES ON SOLVENT EFFECT

Acetic, propionic, butyric, valeric and caproic acids were studied in detail in bromobenzene and chlorobenzene, at different temperatures. The activation parameters for each acid were calculated for both the solvents. For completeness sake, the thermodynamic functions for all the acids in the nitrobenzene reported earlier has been summarized here. The results are presented here, acid wise.

The product gases (SO_2 & HCl) dissolved slightly in chlorobenzene and bromobenzene and somewhat appreciably in nitrobenzene. Therefore these solvents were first saturated with these gases and then stirred well at the experimental temperatures to remove excess gases. The experiments were performed in duplicates and the results were found reproducible within the experimental error.

To see whether it is the dielectric constant of the medium or the solvent nature that is important in determining the solvent effect; the kinetics was followed in xylene (100%) and xylene-dioxane (25% & 75%) mixture. Effluent gases were insoluble in xylene and dioxane.

E X P E R I M E N T A L

The reaction in each case was followed as described earlier using the modified technique of mixing as described earlier. The solvents were purified before use.

Chlorobenzene[109]

Commercial chlorobenzene (B.D.H.) was purified by shaking repeatedly with sulphuric acid till the acid became colourless. It was then washed with water and finally with dilute potassium carbonate solution, and dried with calcium chloride and distilled. The distillate at 131.1°C was collected and it was further dried by keeping it over phosphorous pentaoxide for 24 hours. The liquid was filtered and again distilled in an all glass assembly. The boiling point dropped to 130.7°C while the refractive index did not change.

Bromobenzene

Bromobenzene was (B.D.H.) L.R. reagent and was treated like chlorobenzene.

Xylene[110]

B.D.H. laboratory grade xylene was distilled in an all glass apparatus. The distillate between 137° to 142° was collected and kept moisture protected.

Dioxane[111]

Commercial variety usually contains small quantities of acetaldehyde, appreciable amounts of glycol acetal, together with some water. Upon keeping the acetal tends to undergo hydrolysis and the librated acetaldehyde lead to some peroxide formation. One litre of technical dioxane, 14 ml of concentrated hydrochloric acid, and 10 ml of water were refluxed for 8 hours. Slow stream of nitrogen was bubbled through the solution all the time to remove the acetaldehyde formed. The solution was then cooled and saturated with potassium hydroxide. The aqueous layer was discarded. To remove the remaining water, it was kept over fresh potassium hydroxide pellets for 24 hours and was then refluxed over excess of sodium for 12 hours. Finally, the diethylene dioxide was distilled from sodium at 101.5°/760 mm and the distillate was passed through a column of activated alumina to remove the peroxide. It was stored in coloured bottles.

To determine the solubility of the effluent gases in these solvents, 31.6 ml of gas (HCl & SO_2) at room temperature and pressure was allowed to stand for four hours over 55 ml of the solvent in a rocking burette. 0.2 ml & 0.35 ml of gas was found to dissolve in the xylene and dioxane respectively.

Acetic Acid - Thionyl Chloride reaction

Acetic acid thionyl chloride reaction was studied in xylene and xylene dioxane mixture. The order of the reaction was determined graphically.

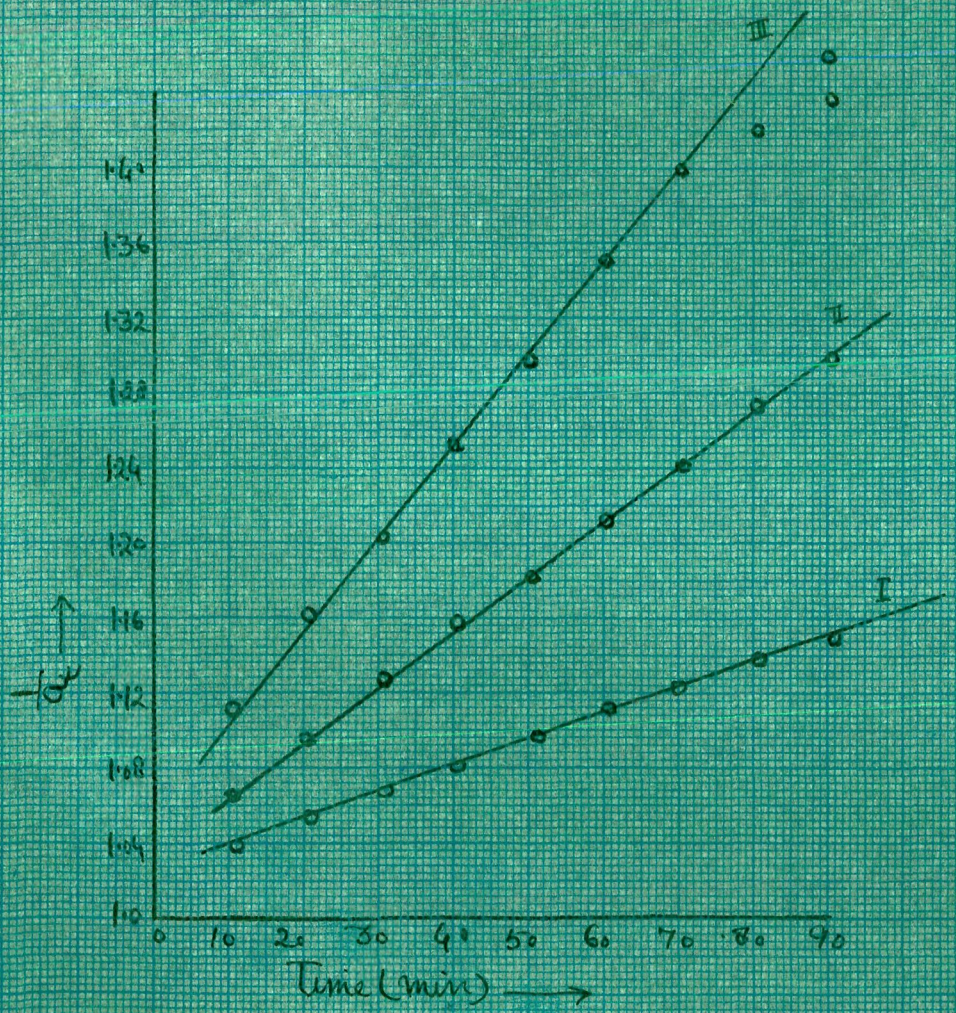


Fig No 35

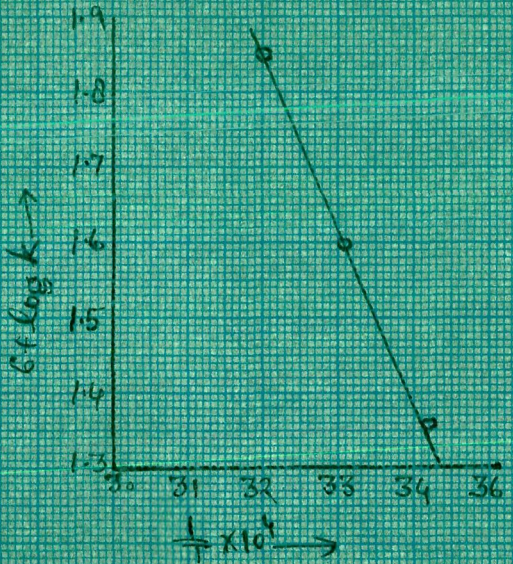


Fig No 36

Acetic Acid - Thionyl Chloride System

Table - 53.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 740.2 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	39.9	"	0.961	"	"
20	49.1	"	0.951	"	"
30	64.3	"	0.936	"	"
40	74.5	"	0.926	"	"
50	88.4	"	0.912	"	"
60	98.2	"	0.902	"	"
70	107.6	"	0.893	"	"
80	120.8	"	0.880	"	"
90	130.0	"	0.871	"	"

Rate constant = 22.9 x 10^{-6} litre mole^{-1} sec^{-1} (Curve I, fig. 35)

Table - 54.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 730.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.0	mole	litre^{-1}
10	49.0	"	0.951	"	"
20	64.3	"	0.936	"	"
30	113.8	"	0.887	"	"
40	136.2	"	0.864	"	"
50	153.4	"	0.848	"	"
60	172.6	"	0.827	"	"
70	193.1	"	0.807	"	"
80	204.5	"	0.796	"	"
90	231.0	"	0.769	"	"

Rete constant = 40 x 10^{-6} litre mole^{-1} sec^{-1} (Curve II, fig. 35)

Table - 55.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 728.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	111.0	"	0.897	" "
20	152.4	"	0.858	" "
30	185.0	"	0.828	" "
40	212.2	"	0.803	" "
50	239.0	"	0.769	" "
60	275.2	"	0.744	" "
70	306.0	"	0.715	" "

Rate constant = 72 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 35)

Table - 56.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 732.9 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
5	25.1	"	0.975	" "
10	35.6	"	0.964	" "
15	43.4	"	0.957	" "
20	50.5	"	0.949	" "
30	62.1	"	0.938	" "
40	71.3	"	0.929	" "
50	80.5	"	0.919	" "
60	91.0	"	0.909	" "
70	98.3	"	0.902	" "
80	105.3	"	0.894	" "
90	112.8	"	0.887	" "

Rate constant = 21.1 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 37)

Table - 57.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 627.7 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$ in chlorobenzene

(Time Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
5	40.3	"	0.966	"	"
10	57.3	"	0.952	"	"
15	71.6	"	0.941	"	"
20	82.8	"	0.931	"	"
30	103.9	"	0.914	"	"
40	121.6	"	0.899	"	"
50	137.6	"	0.886	"	"
60	152.0	"	0.874	"	"
70	165.6	"	0.863	"	"
80	178.2	"	0.833	"	"

Rate constant = 36.6 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 37)

Table - 58.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 709.2 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0.2	ml	1.00	mole	litre^{-1}
5	56.6	"	0.949	"	"
10	82.2	"	0.926	"	"
15	97.7	"	0.912	"	"
20	109.0	"	0.902	"	"
30	150.0	"	0.867	"	"
40	182.3	"	0.835	"	"
50	204.7	"	0.815	"	"
60	224.0	"	0.797	"	"
70	243.4	"	0.769	"	"
80	261.6	"	0.755	"	"
90	274.5	"	0.742	"	"

Rate constant = 65 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 37)

In all cases the rate constants were evaluated from the slopes of time versus concentration inverse plots. The activation parameters were calculated as before. The results are summarized below.

Table - 59.

Activation parameters for acetic acid - thionyl chloride reaction in different solvents.

	Nitrobenzene	Bromobenzene	Chlorobenzene
Energy of activation (E)	10.99 K cals $mole^{-1}$	11.22 K cals $mole^{-1}$	11.22 K cals $mole^{-1}$
Frequency factor (A)	$2 \times 10^5 sec^{-1}$	$4.8 \times 10^4 sec^{-1}$	$4 \times 10^4 sec^{-1}$
Internal energy of activation ($\Delta E^{\neq}$) (at 303^oK)	10.38 K cals $mole^{-1}$	10.6 K cals $mole^{-1}$	10.61 K cals $mole^{-1}$
Free energy of activation ($\Delta F^{\neq}$) (at 303^oK)	23.11 K cals $mole^{-1}$	23.87 K cals $mole^{-1}$	24.0 K cals $mole^{-1}$
Entropy of activation ($\Delta S^{\neq}$) (at 303^oK)	-42.0 e.u.	-43.6 e.u.	-44.1 e.u.

Propionic acid - thionyl chloride system

Table - 60.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 746.7 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	19.6	"	0.981	" "
20	29.3	"	0.971	" "
30	39.1	"	0.962	" "
40	48.8	"	0.952	" "
50	57.0	"	0.943	" "
60	66.2	"	0.934	" "
70	74.5	"	0.926	" "
80	83.8	"	0.917	" "
90	94.0	"	0.907	" "

Rate constant = 16.66×10^{-6} litre mole^{-1}sec^{-1}
(Curve I, fig. 39)

Table - 61.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 741.3 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	37.4	"	0.964	" "
20	58.0	"	0.943	" "
30	73.6	"	0.927	" "
40	86.6	"	0.914	" "
50	98.3	"	0.903	" "
60	109.8	"	0.892	" "
70	120.1	"	0.882	" "
80	135.0	"	0.865	" "
90	146.0	"	0.854	" "

Rate constant = 29.1×10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 39)

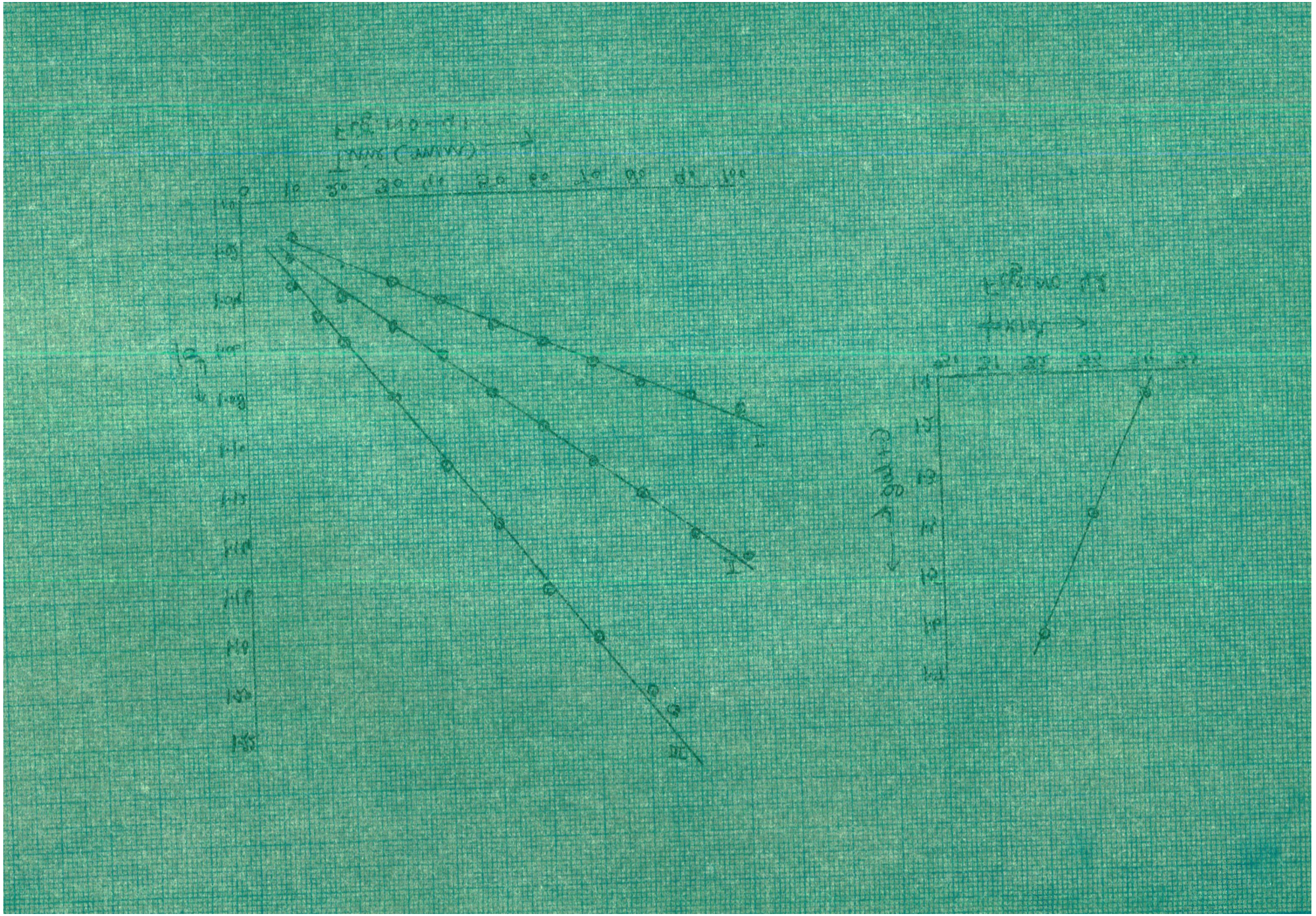


Table - 62.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 735.0 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	56.0	"	0.947	" "
20	89.5	"	0.916	" "
30	115.1	"	0.892	" "
40	134.1	"	0.877	" "
50	155.0	"	0.854	" "
60	173.5	"	0.837	" "
70	188.8	"	0.822	" "
80	202.0	"	0.810	" "
90	213.0	"	0.793	" "

Rate constant = 52 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 39)

Table - 63.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 734.9 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	12.0	"	0.988	" "
20	22.5	"	0.977	" "
30	30.0	"	0.970	" "
40	38.2	"	0.962	" "
50	45.5	"	0.954	" "
60	52.6	"	0.947	" "
70	59.1	"	0.941	" "
80	65.9	"	0.934	" "
90	72.0	"	0.928	" "
100	78.3	"	0.922	" "

Rate constant = 13.9 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 41).

Table - 64.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 745.4 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole litre^{-1}	
10	22.8	"	0.978	"	"
20	40.5	"	0.961	"	"
30	55.3	"	0.947	"	"
40	68.0	"	0.935	"	"
50	79.8	"	0.923	"	"
60	90.6	"	0.913	"	"
70	102.0	"	0.902	"	"
80	112.0	"	0.890	"	"
90	128.9	"	0.876	"	"
100	137.0	"	0.869	"	"

Rate constant = 24 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 41)

Table - 65.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 712.4 mm
Reaction mixture: 10 ml each CH_3CH_2COOH & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole litre^{-1}	
5	21.3	"	0.981	"	"
10	37.3	"	0.966	"	"
20	65.5	"	0.943	"	"
30	87.4	"	0.925	"	"
40	108.2	"	0.903	"	"
50	127.1	"	0.884	"	"
60	145.3	"	0.862	"	"
70	161.1	"	0.847	"	"
80	176.8	"	0.841	"	"
90	190.8	"	0.828	"	"
100	204.0	"	0.816	"	"

Rate constant = 41.7 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve III, fig. 41)

Table - 66.

Activation parameters for propionic acid - thionyl chloride reaction in different solvents.

	Nitrobenzene	Bromobenzene	Chlorobenzene
Energy of Activation (E)	11.22 K cals $mole^{-1}$	11.45 K cals $mole^{-1}$	11.0 K cals $mole^{-1}$
Frequency factor (A)	$3.98 \times 10^{-4} sec^{-1}$	$5 \times 10^{-4} sec^{-1}$	3.5×10^{-4} sec^{-1}
Internal energy of activation ($\Delta E^{\neq}$) (at 303°K)	10.61 K cals $mole^{-1}$	10.84 K cals $mole^{-1}$	10.38 K cals $mole^{-1}$
Free energy of activation ($\Delta F^{\neq}$) (at 303°K)	23.36 K cals $mole^{-1}$	24.07 K cals $mole^{-1}$	24.2 K cals $mole^{-1}$
Entropy of activation ($\Delta S^{\neq}$) (at 303°K)	-42.0 e.u.	- 43.6 e.u.	-45.6 e.u.

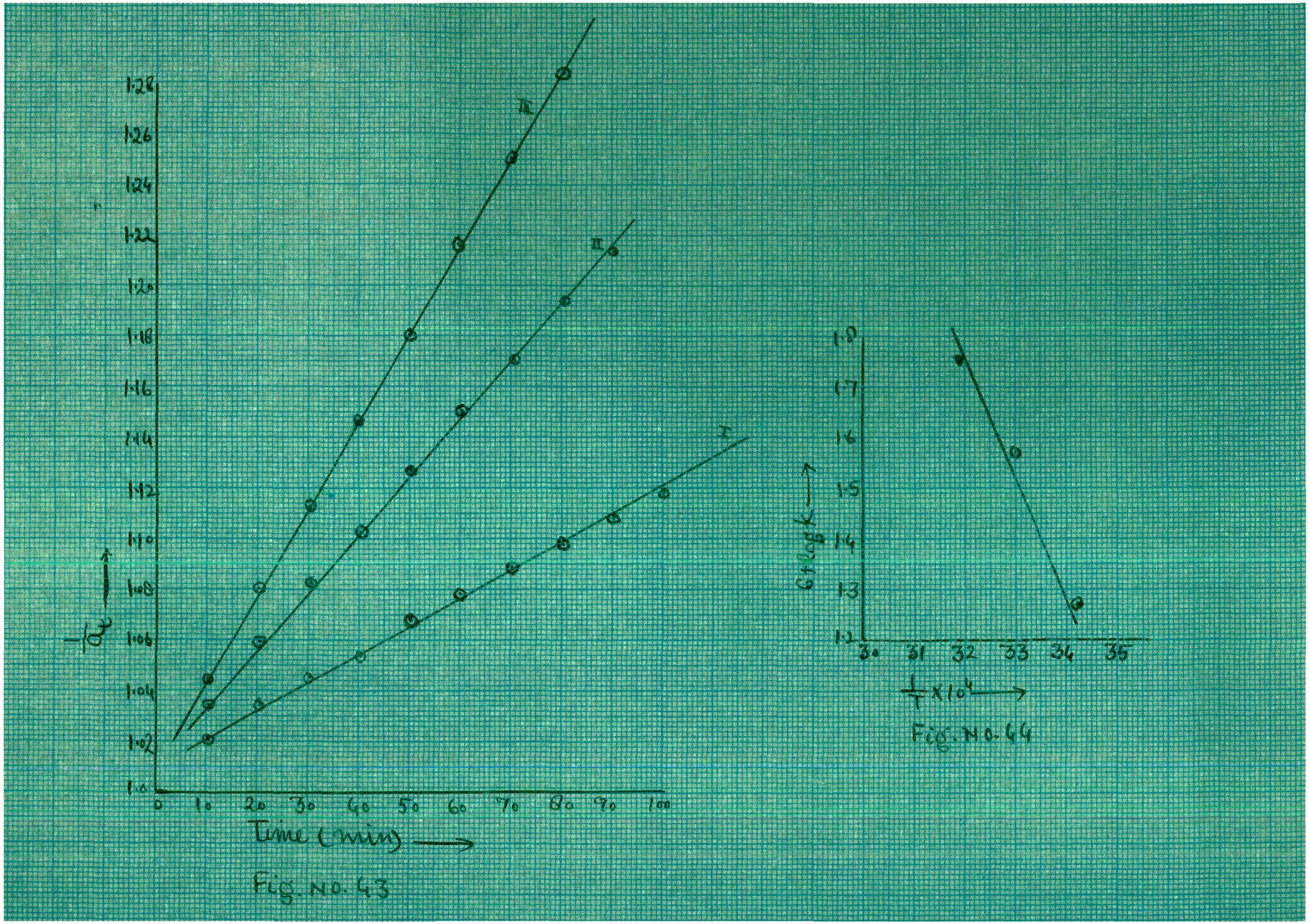


Fig. No. 43

Fig. No. 44

Butyric acid - thionyl chloride system

Table - 67.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 740.3 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole litre^{-1}	
10	19.5	"	0.981	"	"
20	33.0	"	0.967	"	"
30	44.1	"	0.956	"	"
40	51.0	"	0.949	"	"
50	62.7	"	0.937	"	"
60	72.7	"	0.927	"	"
70	79.8	"	0.920	"	"
80	87.7	"	0.912	"	"
90	94.7	"	0.905	"	"
100	101.9	"	0.898	"	"
110	108.7	"	0.891	"	"

Rate constant = 18.5 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve I, fig. 43)

Table - 68.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 730.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole litre^{-1}	
10	30.9	"	0.971	"	"
20	46.8	"	0.956	"	"
30	66.0	"	0.938	"	"
40	70.0	"	0.922	"	"
50	100.0	"	0.906	"	"
60	107.4	"	0.899	"	"
70	130.9	"	0.877	"	"
80	145.7	"	0.862	"	"
90	161.7	"	0.848	"	"

Rate constant = 37.5 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 43)

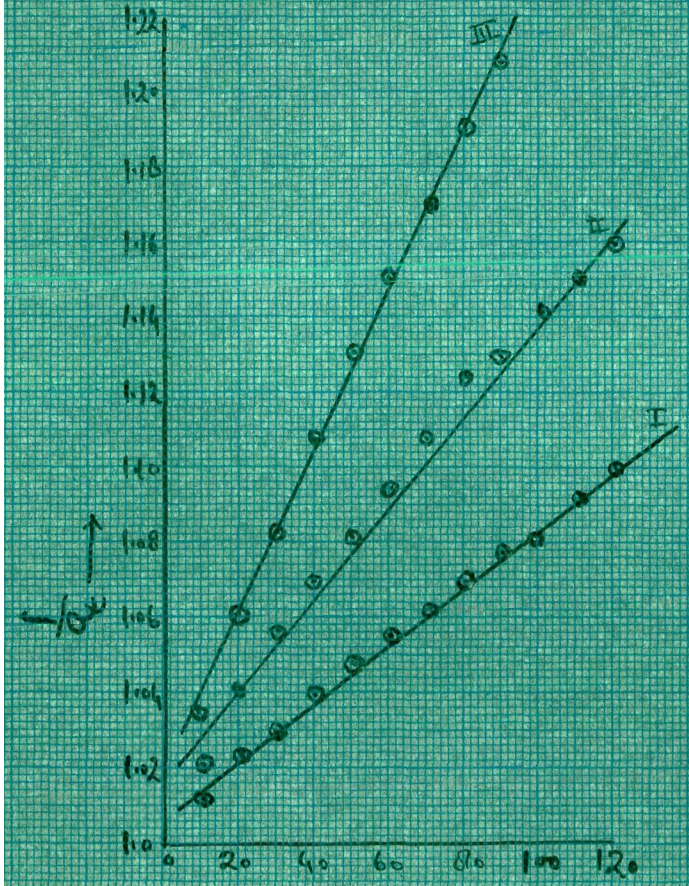


Fig. NO. 45

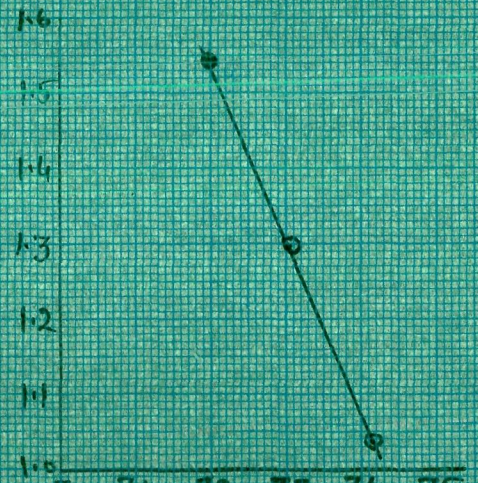


Fig. NO. 46

Table - 69.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 730.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	48.5	"	0.956	"	"
20	78.7	"	0.926	"	"
30	107.4	"	0.899	"	"
40	137.2	"	0.871	"	"
50	152.1	"	0.848	"	"
60	179.9	"	0.822	"	"
70	212.8	"	0.800	"	"
80	233.0	"	0.781	"	"
90	240.0	"	0.775	"	"

Rate constant = 56.6×10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 43)

Table - 70.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 730.8 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	12.0	"	0.988	"	"
20	22.5	"	0.977	"	"
30	30.0	"	0.970	"	"
40	38.2	"	0.962	"	"
50	45.5	"	0.954	"	"
60	52.6	"	0.947	"	"
70	59.1	"	0.941	"	"
80	65.9	"	0.934	"	"
90	72.0	"	0.928	"	"
100	78.3	"	0.922	"	"
110	83.5	"	0.916	"	"
120	88.8	"	0.901	"	"

Rate constant = 10.96×10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 45)

Table - 71.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 726.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
5	12.5	"	0.988	" "
10	22.8	"	0.978	" "
20	40.5	"	0.961	" "
30	55.3	"	0.947	" "
40	68.0	"	0.935	" "
50	79.8	"	0.923	" "
60	90.6	"	0.913	" "
70	102.0	"	0.903	" "
80	111.2	"	0.890	" "
100	128.9	"	0.876	" "
110	137.0	"	0.869	" "

Rate constant = 20.3×10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 45)

Table - 72.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 711.0 mm
Reaction mixture : 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
5	21.3	"	0.981	" "
10	37.3	"	0.966	" "
15	52.1	"	0.953	" "
20	65.5	"	0.943	" "
30	87.4	"	0.925	" "
40	108.2	"	0.903	" "
50	127.1	"	0.884	" "
60	145.3	"	0.862	" "
70	161.1	"	0.847	" "
80	176.8	"	0.841	" "
90	190.8	"	0.828	" "
100	204.0	"	0.816	" "

Rate constant = 35×10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 45)

Table - 73.

Activation parameters for butyric acid - thionyl chloride reaction in different solvents.

	Nitrobenzene	Bromobenzene	Chlorobenzene
Activation energy (E)	11.45 K cals $mole^{-1}$	11.45 K cals $mole^{-1}$	11.45 K cals $mole^{-1}$
Frequency factor (A)	1.4×10^5 sec^{-1}	6.3×10^4 sec^{-1}	3.2×10^4 sec^{-1}
Internal energy of activation ($\Delta E^{\ddagger}$)(at $303^{o}K$)	10.84 K cals $mole^{-1}$	10.84 K cals $mole^{-1}$	10.84 K cals $mole^{-1}$
Free energy of activation ($\Delta F^{\ddagger}$) (at $303^{o}K$)	23.4 K cals $mole^{-1}$	23.9 K cals $mole^{-1}$	24.3 K cals $mole^{-1}$
Entropy of activation ($\Delta S^{\ddagger}$) (at $303^{o}K$)	- 41.4 e.u.	-43.1 e.u.	- 44.4 e.u.

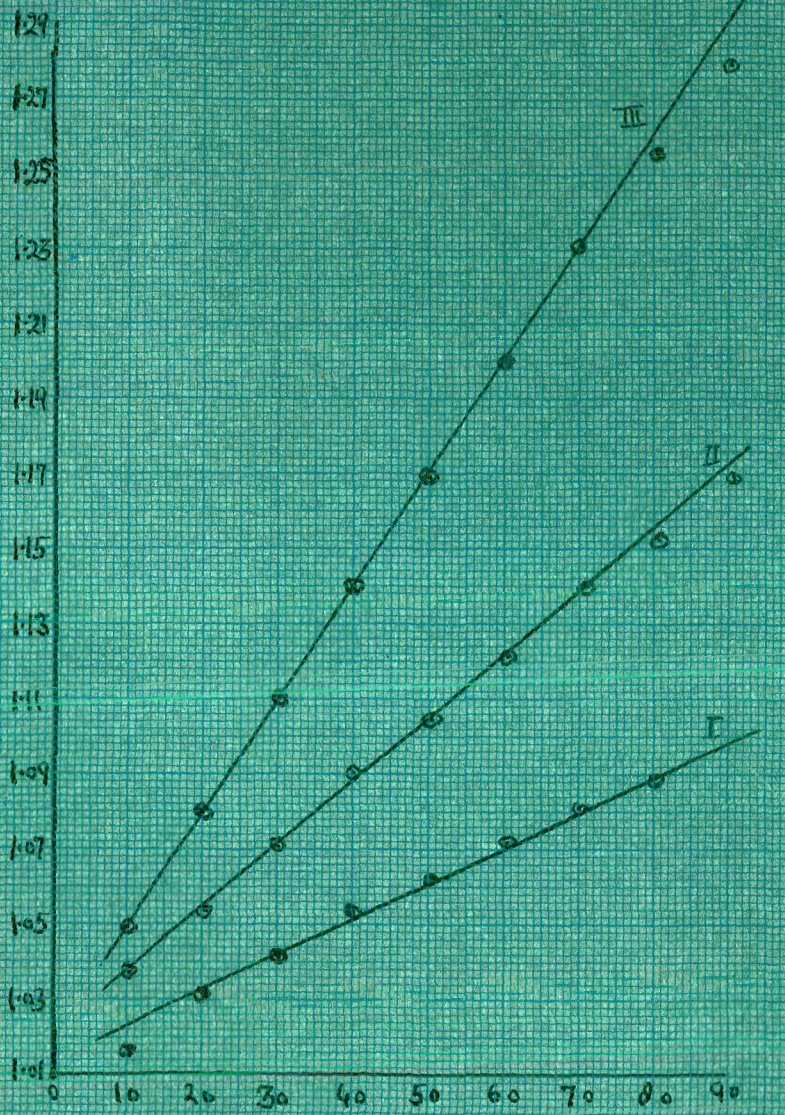


Fig NO 47

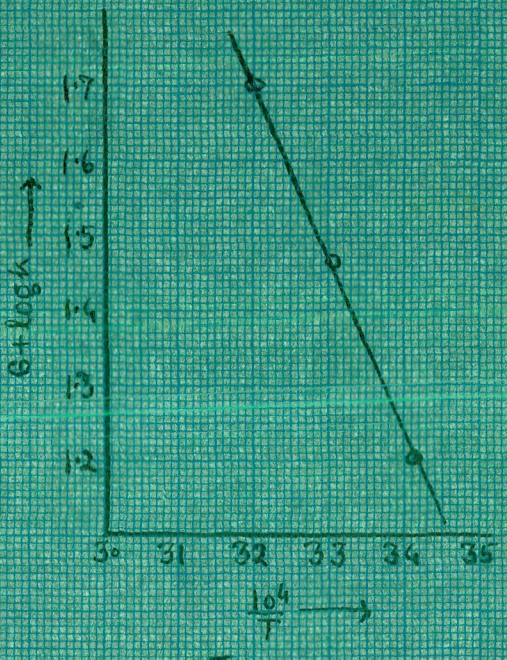


Fig NO 48

Valeric acid - Thionyl chloride system

Table - 74.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 739.4 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	10.0	"	0.982	"	"
20	30.8	"	0.969	"	"
30	41.3	"	0.957	"	"
40	50.7	"	0.949	"	"
50	59.4	"	0.941	"	"
60	67.8	"	0.932	"	"
70	74.9	"	0.925	"	"
80	82.0	"	0.918	"	"
90	89.9	"	0.910	"	"
100	96.4	"	0.903	"	"
110	102.4	"	0.894	"	"
120	108.9	"	0.891	"	"

Rate constant = 16 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 47).

Table - 75.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 735.6 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	31.2	"	0.962	"	"
20	53.0	"	0.949	"	"
30	70.0	"	0.932	"	"
40	85.2	"	0.917	"	"
60	113.0	"	0.891	"	"
70	126.7	"	0.877	"	"
80	137.0	"	0.867	"	"
90	148.2	"	0.856	"	"
100	157.2	"	0.848	"	"
110	167.0	"	0.838	"	"

Rate constant = 28.7 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 47)

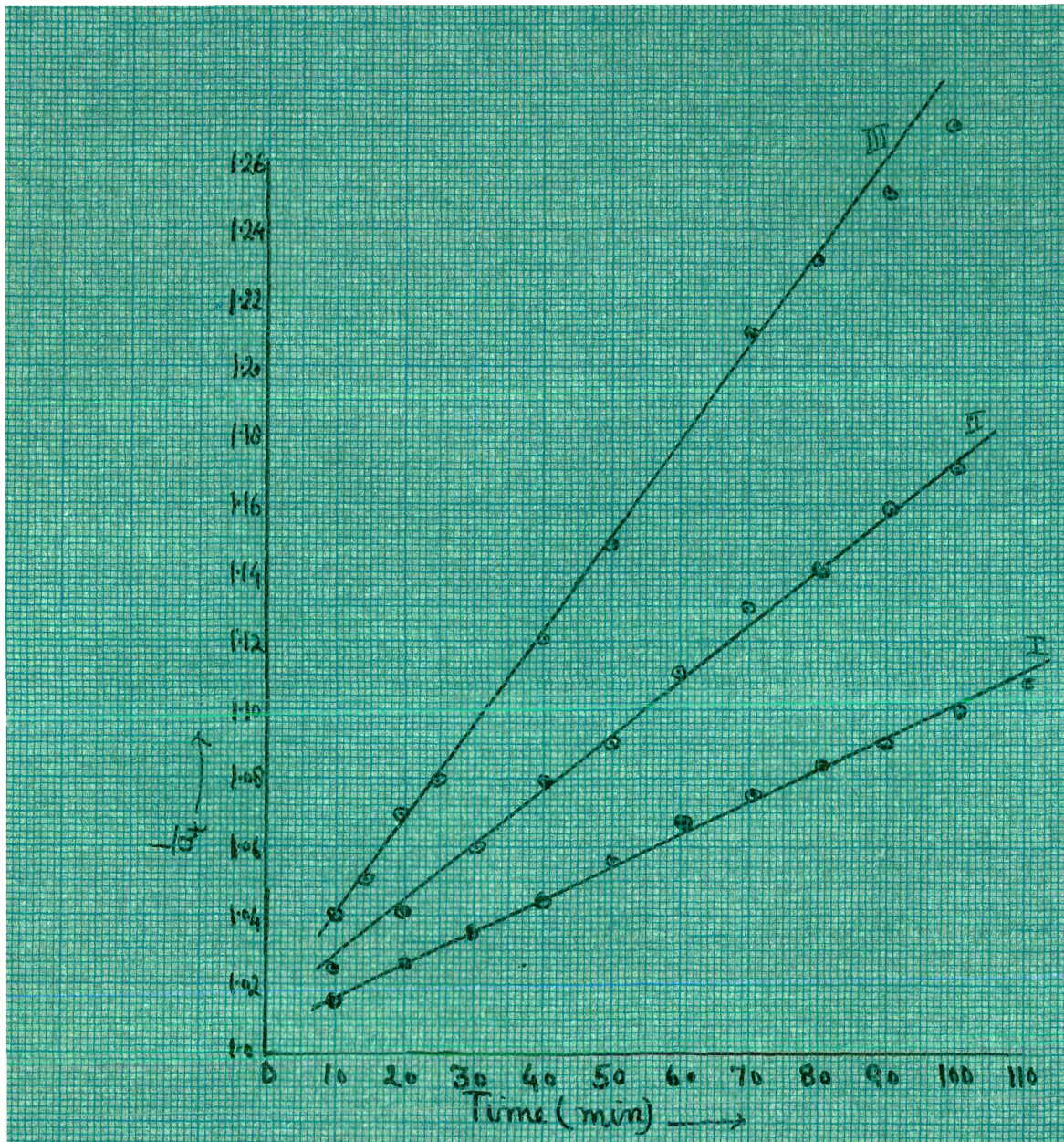


Fig. No. 4a

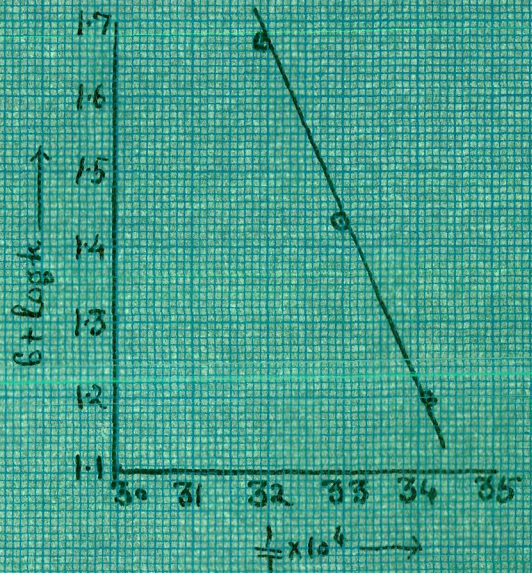


Fig. No. 5a

Table - 76.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 732.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	51.0	"	0.952	"	"
20	78.7	"	0.926	"	"
30	106.5	"	0.900	"	"
40	130.0	"	0.878	"	"
50	155.3	"	0.854	"	"
60	177.6	"	0.833	"	"
70	198.9	"	0.813	"	"
80	220.0	"	0.793	"	"
90	239.2	"	0.775	"	"

Rate constant = 50.0×10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 47)

Table - 77.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 732.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	16.7	"	0.983	"	"
20	27.7	"	0.972	"	"
30	37.5	"	0.962	"	"
40	46.6	"	0.953	"	"
50	55.4	"	0.945	"	"
60	63.4	"	0.937	"	"
70	70.4	"	0.930	"	"
80	77.5	"	0.922	"	"
90	85.5	"	0.915	"	"
100	92.0	"	0.908	"	"
110	97.1	"	0.903	"	"
120	103.4	"	0.897	"	"

Rate constant = 15.8×10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 49)

Table - 78.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 723.1 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole litre^{-1}	
10	24.8	"	0.976	"	"
20	43.4	"	0.968	"	"
30	59.2	"	0.943	"	"
40	72.4	"	0.930	"	"
50	85.2	"	0.918	"	"
60	97.2	"	0.907	"	"
70	108.8	"	0.896	"	"
80	120.0	"	0.885	"	"
90	130.8	"	0.874	"	"
100	142.0	"	0.864	"	"
110	149.8	"	0.857	"	"

Rate constant = 26.8 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 49)

Table - 79.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 706.2 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2M $SOCl_2$ in chlorobenzene

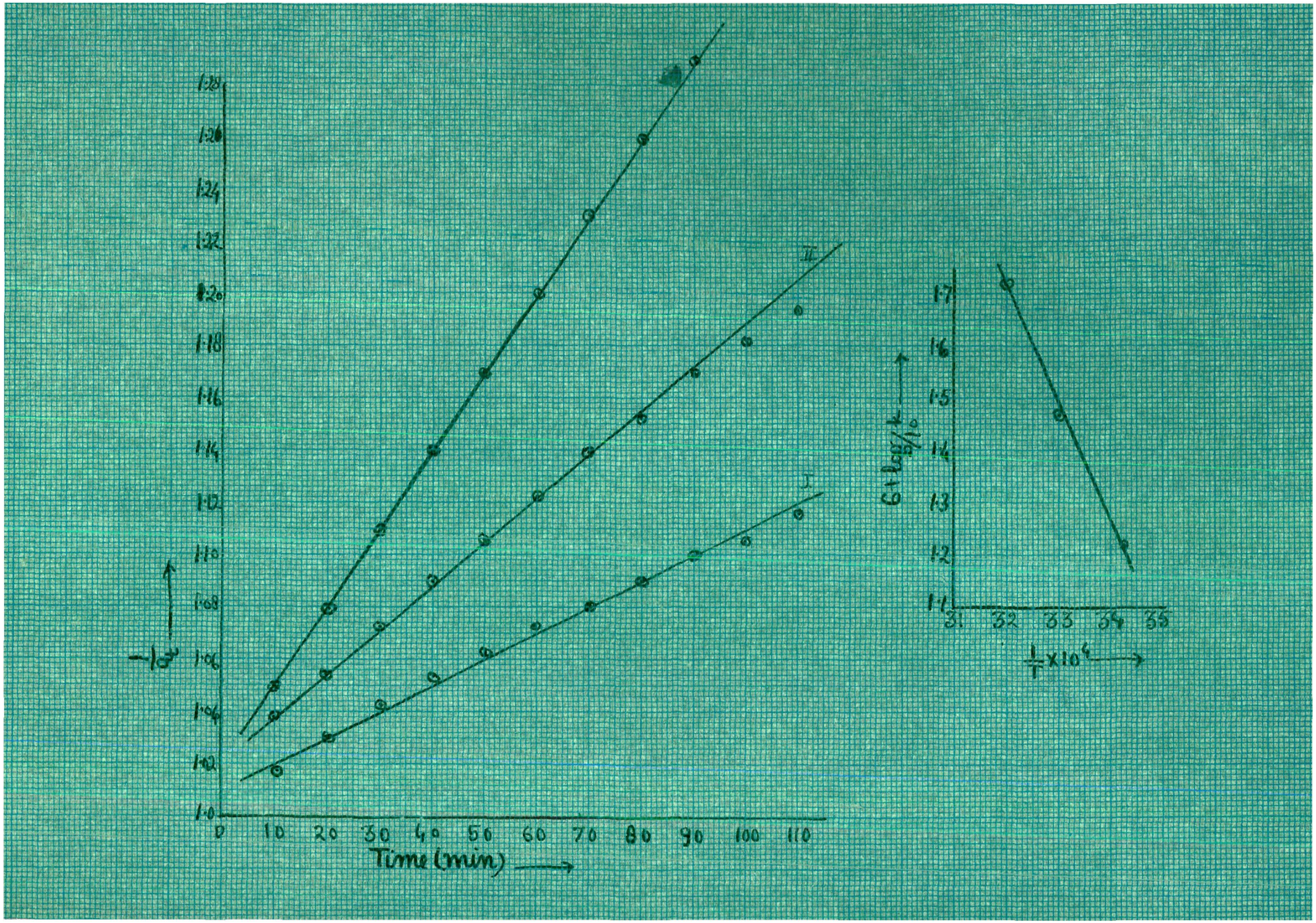
Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole litre^{-1}	
10	39.5	"	0.964	"	"
15	56.7	"	0.949	"	"
20	70.6	"	0.936	"	"
25	83.6	"	0.925	"	"
30	96.6	"	0.913	"	"
40	119.3	"	0.893	"	"
50	139.3	"	0.875	"	"
60	176.3	"	0.841	"	"
70	193.6	"	0.826	"	"
80	209.6	"	0.811	"	"
90	223.6	"	0.799	"	"
100	237.2	"	0.787	"	"

Rate constant = 46.6 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 49)

Table - 80.

Activation parameters for valeric acid acid-thionyl chloride reaction in different solvents.

	Nitrobenzene	Bromobenzene	Chlorobenzene
Activation energy (E)	11.22 K cals $mole^{-1}$	11.22 K cals $mole^{-1}$	11.45 K cals $mole^{-1}$
Frequency factor (A)	10 x 10^4 sec^{-1}	3.4 x 10^4 sec^{-1}	3.2 x 10^4 sec^{-1}
Internal energy of activation ($\Delta E^{\ddagger}$) (at 303°K)	10.61 K cals $mole^{-1}$	10.61 K cals $mole^{-1}$	10.84 K cals $mole^{-1}$
Free energy of activation ($\Delta F^{\ddagger}$) (at 303°K)	23.4 K cals $mole^{-1}$	24.07 K cals $mole^{-1}$	24.2 K cals $mole^{-1}$
Entropy of activation ($\Delta S^{\ddagger}$) (at 303°K)	-42.2 e.u.	-43.4 e.u.	-44.6 e.u.


1·28
1·26
1·24
1·22
1·20
1·18
1·16
1·14
1·12
1·10
1·08
1·06
1·04
1·02
1·0
$-\log\frac{a}{a-x}$
0 10 20 30 40 50 60 70 80 90 100 110
Time (min) ⟶
III
II
I
1·7
1·6
1·5
1·4
1·3
1·2
1·1
$t_{1/2}$ (min) ⟶
31 32 33 34 35
$\frac{1}{T} \times 10^2$ ⟶

Caproic Acid - Thionyl Chloride System

Table - 81.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 738.7 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_4COOH$ & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	11.2 "	0.982 " "
20	31.2 "	0.969 " "
30	41.8 "	0.957 " "
40	51.6 "	0.949 " "
50	60.1 "	0.941 " "
60	68.3 "	0.932 " "
70	75.3 "	0.925 " "
80	82.8 "	0.918 " "
90	91.2 "	0.910 " "
100	97.3 "	0.903 " "
110	103.4 "	0.894 " "
120	109.8 "	0.891 " "

Rate constant = 16.6 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve I, fig. 51)

Table - 82.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 735.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_4COOH$ & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	32.2 "	0.963 " "
20	54.6 "	0.950 " "
30	71.8 "	0.933 " "
40	86.8 "	0.918 " "
50	98.9 "	0.905 " "
60	113.0 "	0.892 " "
70	128.2 "	0.879 " "
80	139.6 "	0.868 " "
90	150.2 "	0.849 " "
100	159.8 "	0.839 " "

Rate constant = 29.8 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 51)

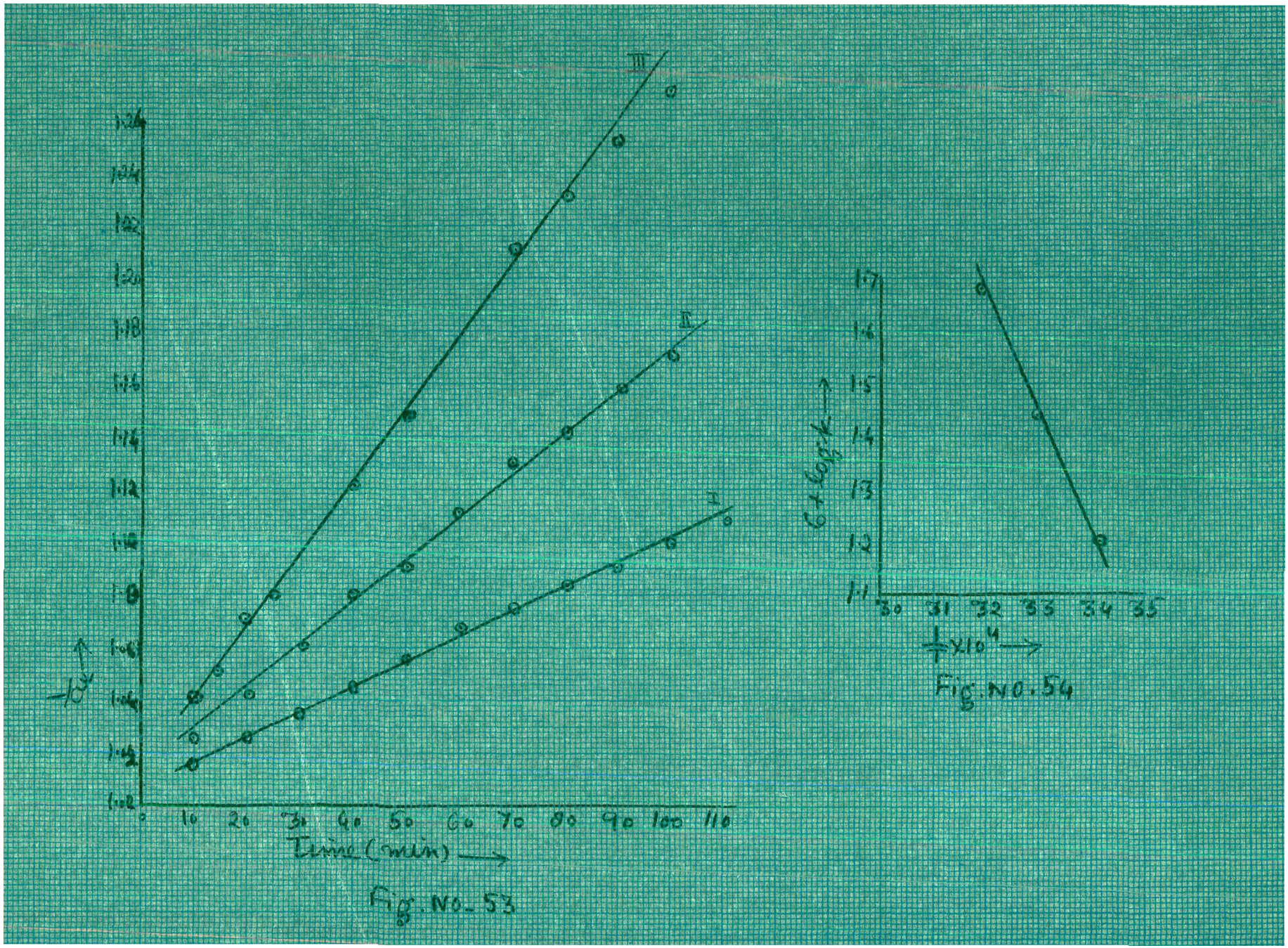


Fig. No. 53

Fig. No. 54

Table - 83.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 739.2 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_4COOH$ & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	51.0 "	0.952 " "
20	79.0 "	0.927 " "
30	107.2 "	0.901 " "
40	130.8 "	0.879 " "
50	155.8 "	0.856 " "
60	178.0 "	0.835 " "
70	199.2 "	0.815 " "
80	221.5 "	0.800 " "
90	240.3 "	0.777 " "

Rate constant = 50.6 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 51)

Table - 84.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 732.2 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_4COOH$ & 2M $SOCl_2$ in chlorobenzene

Time (Min)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	15.8 "	0.982 " "
20	26.6 "	0.971 " "
30	37.0 "	0.961 " "
40	44.9 "	0.953 " "
50	53.9 "	0.944 " "
60	62.4 "	0.936 " "
70	69.5 "	0.930 " "
80	76.3 "	0.922 " "
90	85.0 "	0.914 " "
100	92.3 "	0.909 " "
110	97.2 "	0.904 " "
120	102.8 "	0.895 " "

Rate constant = 15.6 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 53)

Table - 85.

Reaction bath temperature = $30 \pm 0.1^{\circ}C$
Mean atmospheric pressure = 735.8 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_4COOH$ & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	24.0	"	0.975	" "
20	42.4	"	0.968	" "
30	58.8	"	0.943	" "
40	71.5	"	0.929	" "
50	84.5	"	0.918	" "
60	96.3	"	0.908	" "
70	107.8	"	0.897	" "
80	118.8	"	0.885	" "
90	129.9	"	0.874	" "
100	141.2	"	0.863	" "
110	148.9	"	0.857	" "

Rate constant = 26.3×10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 53)

Table - 86.

Reaction bath temperature = $40 \pm 0.1^{\circ}C$
Mean atmospheric pressure = 735.6 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_4COOH$ & 2M $SOCl_2$ in chlorobenzene

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	38.4	"	0.965	" "
20	69.7	"	0.935	" "
30	94.5	"	0.914	" "
40	117.2	"	0.893	" "
50	138.6	"	0.875	" "
60	176.5	"	0.842	" "
70	193.0	"	0.826	" "
80	208.9	"	0.812	" "
90	222.5	"	0.800	" "
100	236.8	"	0.787	" "

Rate constant = 46×10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 53)

Table - 87.

Activation parameters for n-caproic acid-thionyl chloride reaction in different solvents

	Nitrobenzene	Bromobenzene	Chlorobenzene
Energy of activation (E)	11.0 K cals $mole^{-1}$	11.22 K cals $mole^{-1}$	11.45 K cals $mole^{-1}$
Frequency factor (A)	7.58×10^4 sec^{-1}	3.6×10^4 sec^{-1}	3.3×10^4 sec^{-1}
Internal energy of activation ($\Delta E^{\ddagger}$) (at 303°K)	10.38 K cals $mole^{-1}$	10.61 K cals $mole^{-1}$	10.84 K cals $mole^{-1}$
Free energy of activation ($\Delta F^{\ddagger}$) (at 303°K)	23.32 K cals $mole^{-1}$	24.0 K cals $mole^{-1}$	24.3 Kcals $mole^{-1}$
Entropy of activation($\Delta S^{\ddagger}$) (at 303°K)	-42.7 e.u.	-43.4 e.u.	-44.8 e.u.

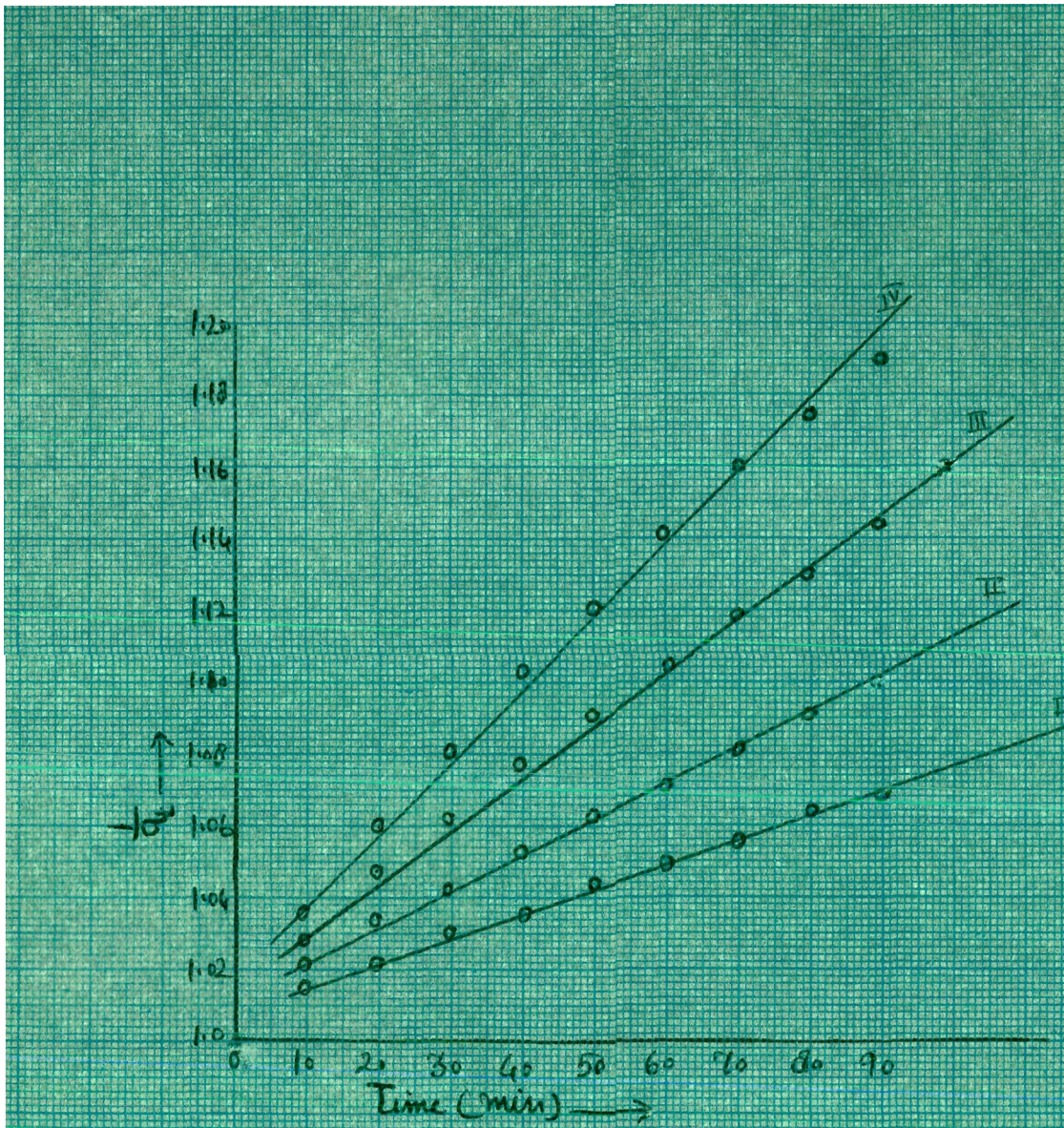


Fig NO 55

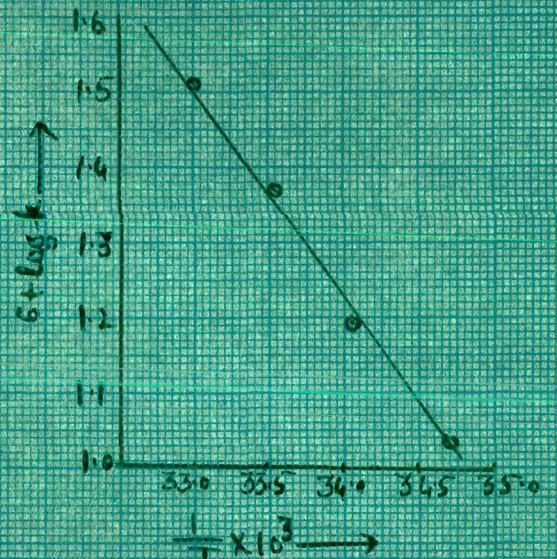


Fig NO 56

Acetic acid - thionyl chloride reaction

Studies in Xylene

Table - 88.

Reaction bath temperature = 15 ± 0.1°C
Mean atmospheric pressure = 749.5 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	13.7	"	0.985	" "
20	21.1	"	0.978	" "
30	27.6	"	0.971	" "
40	33.4	"	0.965	" "
50	39.6	"	0.953	" "
60	44.9	"	0.958	" "
70	50.1	"	0.953	" "
80	55.8	"	0.939	" "
90	61.7	"	0.935	" "

Rate constant = 11.3 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve I, fig. 55)

Table - 89.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 766.8 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	21.3	"	0.978	" "
20	31.3	"	0.968	" "
30	40.5	"	0.959	" "
40	49.1	"	0.950	" "
50	57.1	"	0.941	" "
60	65.1	"	0.933	" "
70	72.4	"	0.925	" "
80	80.0	"	0.918	" "

Rate constant = 16.0 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 55)

Table - 90.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 746.5 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.0 mole litre^{-1}
10	27.9 "	0.972 " "
20	42.5 "	0.955 " "
30	58.7 "	0.941 " "
40	71.5 "	0.928 " "
50	83.5 "	0.916 " "
60	95.1 "	0.904 " "
70	105.5 "	0.894 " "
80	115.6 "	0.883 " "
90	126.0 "	0.874 " "

Rate constant = 24 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve III, fig. 55)

Table - 91.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 750.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	35.3 "	0.964 " "
20	57.7 "	0.942 " "
30	75.7 "	0.925 " "
40	94.5 "	0.906 " "
50	110.0 "	0.891 " "
60	125.3 "	0.875 " "
70	138.3 "	0.863 " "
80	150.3 "	0.851 " "
90	161.5 "	0.840 " "

Rate constant = 33.3 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve IV, fig. 55)

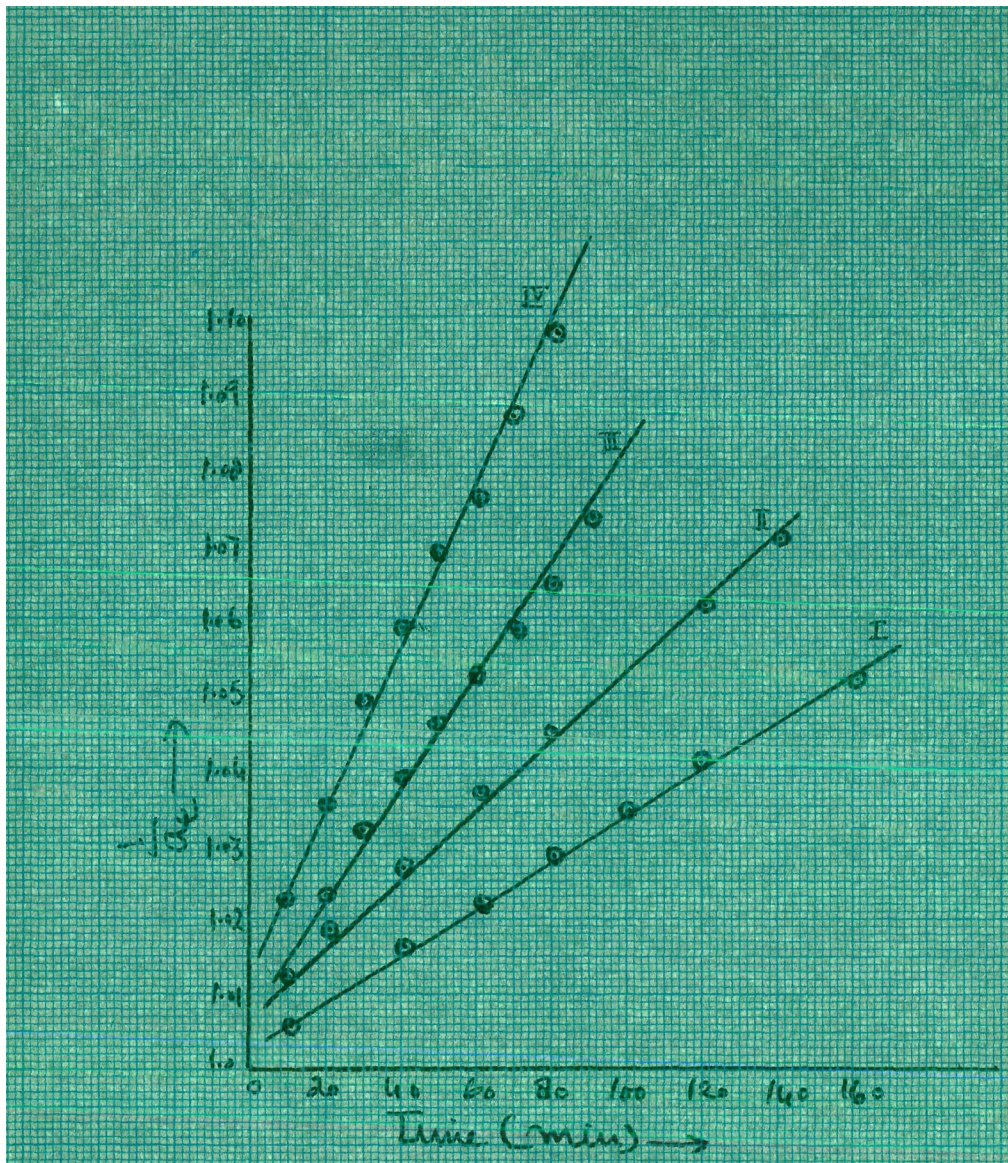


Fig. No. 57

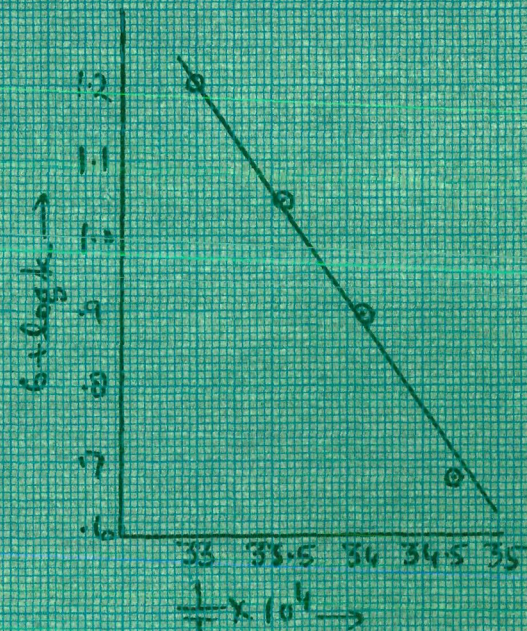


Fig. No. 58

The activation energy E & the other thermodynamic functions given below were calculated as before.

E = 12.2 Kcals $mole^{-1}$

$\Delta E^{\neq}$ = 11.6 Kcals $mole^{-1}$

$\Delta S^{\neq}$ = -42.3 e.u.

log A = 3.23

Studies in Xylene (75%) —— dioxane (25%) mixture:

Xylene-dioxane mixture was prepared by volume. The studies were made as before and the results are recorded below.

Table - 92.

Reaction bath temperature = 15 ± 0.1°C
Mean atmospheric pressure = 743.7 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.0 mole litre^{-1}
10	6.0 "	0.993 " "
20	9.6 "	0.989 " "
40	15.2 "	0.983 " "
60	20.5 "	0.978 " "
80	23.8 "	0.974 " "
100	30.0. "	0.967 " "
120	35.4 "	0.962 " "
140	40.0 "	0.957 " "
160	44.6 "	0.953 " "

Rate constant = 4.6 x 10^{-6} litre $mole^{-1} sec^{-1}$
(Curve I, fig. 57)

Table - 93.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 744.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	2.6	ml	0.998	mole	litre^{-1}
10	11.3	"	0.989	"	"
20	17.6	"	0.983	"	"
40	26.5	"	0.973	"	"
60	35.8	"	0.964	"	"
80	42.2	"	0.957	"	"
100	50.8	"	0.950	"	"
120	59.0	"	0.942	"	"
140	66.8	"	0.934	"	"

Rate constant = 7.93×10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 57)

Table - 94.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 743.6 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	3.2	ml	0.993	mole	litre^{-1}
10	14.0	"	0.980	"	"
20	23.2	"	0.976	"	"
30	31.8	"	0.968	"	"
40	37.9	"	0.962	"	"
50	44.5	"	0.955	"	"
60	50.3	"	0.949	"	"
70	55.6	"	0.944	"	"
80	60.9	"	0.939	"	"
90	66.7	"	0.931	"	"

Rate constant = 11.4×10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 57)

Table - 95.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 744.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.0 mole litre^{-1}
10	23.5 "	0.975 " "
20	36.9 "	0.965 " "
30	48.5 "	0.952 " "
40	56.4 "	0.944 " "
50	65.0 "	0.936 " "
60	73.0 "	0.928 " "
70	81.0 "	0.920 " "
80	89.0 "	0.911 " "
90	96.8 "	0.902 " "

Rate constant = 16.1×10^{-6} litre mole^{-1} sec^{-1}
(Curve IV, fig. 57)

The parameters of activation were evaluated at 303°K. The following are the values.

E = 12.8 Kcals mole^{-1}

$\Delta E^{\ddagger}$ = 12.2 Kcals mole^{-1}

$\Delta F^{\ddagger}$ = 24.4 Kcals mole^{-1}

$\Delta S^{\ddagger}$ = -40.3 2.u.

$\log_{10} A$ = 4.45

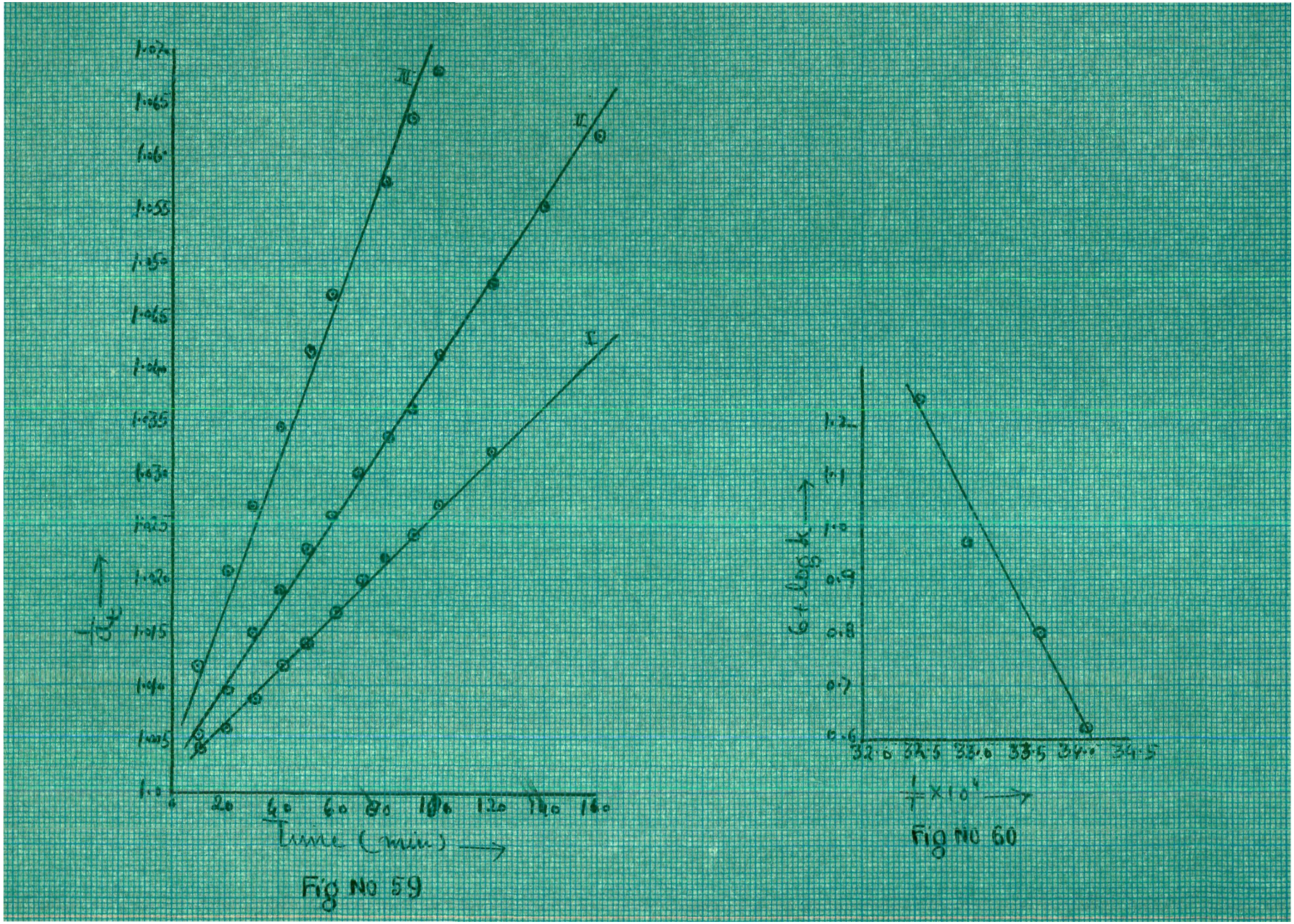


Fig No 59

Fig No 60

Studies in Xylene (50%) —— dioxane (50%) mixture

As before, the mixture was prepared by volume and the kinetics was followed at various temperatures to determine the activation parameters.

Table - 96.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 743.6 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.0 mole litre^{-1}
10	4.5 "	0.996 " "
20	5.2 "	0.995 " "
40	12.4 "	0.988 " "
60	17.3 "	0.983 " "
80	21.7 "	0.978 " "
100	26.5 "	0.974 " "
120	31.3 "	0.969 " "
140	35.8 "	0.964 " "
160	40.3 "	0.961 " "

Rate constant = 4.2 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 59)

Table - 97.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 743.5 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.0 mole litre^{-1}
10	6.5 "	0.994 " "
20	11.0 "	0.989 " "
40	19.0 "	0.981 " "
60	26.1 "	0.974 " "
80	31.8 "	0.969 " "
100	39.2 "	0.961 " "
120	46.3 "	0.954 " "
140	52.8 "	0.948 " "
160	59.2 "	0.942 " "

Rate constant = 6.4 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 59)

Table - 98.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 744.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.0	mole	litre^{-1}
10	13.0	"	0.988	"	"
20	21.8	"	0.979	"	"
40	24.9	"	0.966	"	"
60	46.0	"	0.955	"	"
80	55.3	"	0.946	"	"
100	64.2	"	0.936	"	"
120	68.4	"	0.931	"	"
140	72.5	"	0.928	"	"
160	76.6	"	0.924	"	"

Rate constant = 9.4×10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 59)

Table - 99.

Reaction bath temperature = 35 ± 0.1°C
Mean atmospheric pressure = 741.5 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.0	mole	litre^{-1}
10	18.3	"	0.983	"	"
20	25.4	"	0.976	"	"
40	29.4	"	0.962	"	"
60	46.4	"	0.955	"	"
80	56.6	"	0.945	"	"
100	66.2	"	0.935	"	"
120	73.8	"	0.926	"	"
140	82.2	"	0.916	"	"
160	90.8	"	0.907	"	"

Rate constant = 13.3×10^{-6} litre mole^{-1} sec^{-1}
(Curve IV, fig. 59)

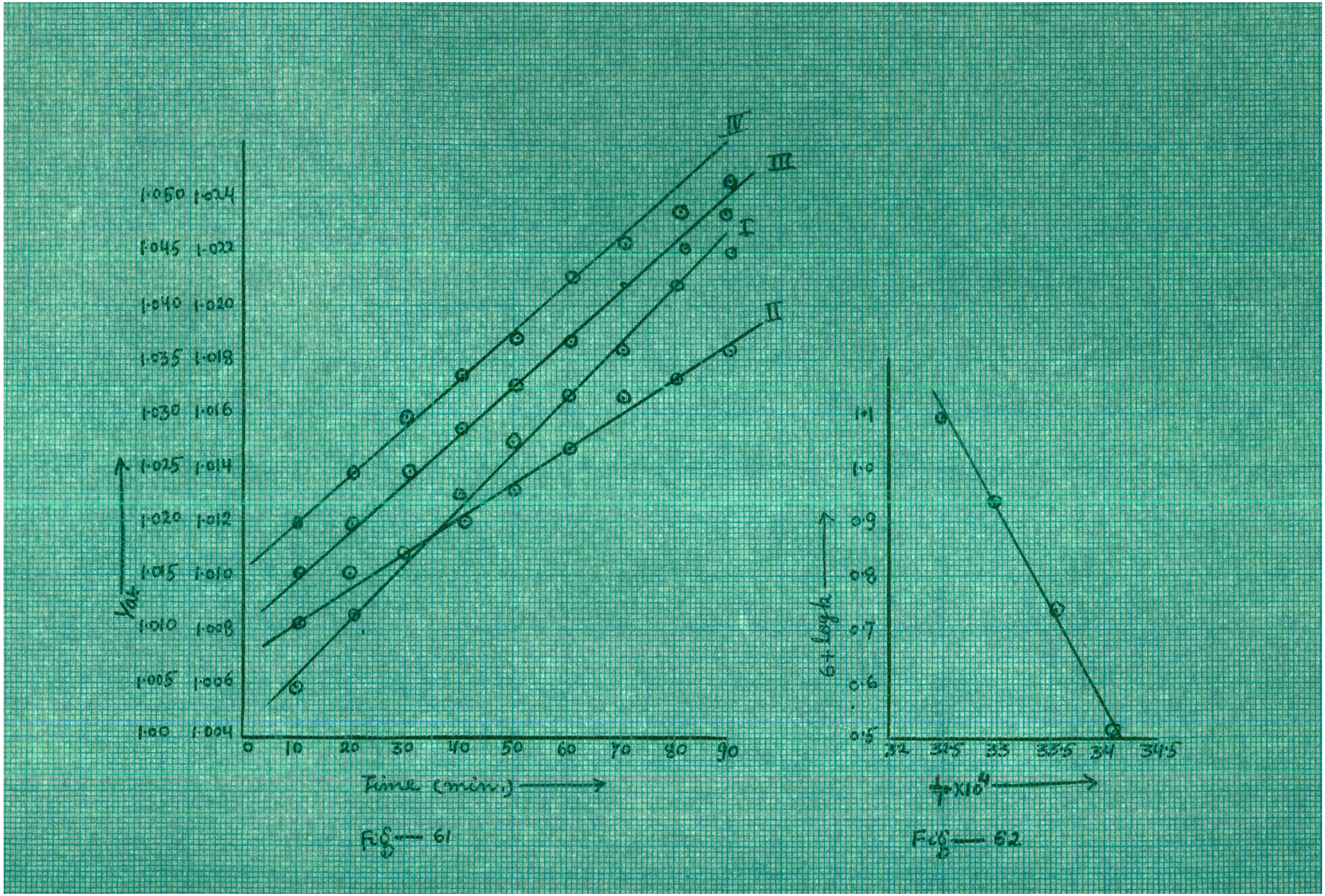

IV
III
II
I
1·050 1·024
1·045 1·022
1·040 1·020
1·035 1·018
1·030 1·016
1·025 1·014
1·020 1·012
1·015 1·010
1·010 1·008
1·005 1·006
1·00 1·004
Volt
0 10 20 30 40 50 60 70 80 90
Time (min.) ⟶
1·1
1·0
0·9
0·8
0·7
0·6
0·5
log I + log k
3·2 3·25 3·3 3·35 3·4 3·45
1/T × 10⁴ ⟶

Fig — 61

Fig — 62

The activation parameters calculated as before are as follows:

E = 13.4 K cals $mole^{-1}$

$\Delta E^{\ddagger}$ = 12.8 K cals $mole^{-1}$

$\Delta F^{\ddagger}$ = 24.7 K cals $mole^{-1}$

$\Delta S^{\ddagger}$ = -39.2 e.u.

$\log_{10}A$ = 4.791

Studies in Xylene (25%) —— dioxane (75%) mixture

The mixture was prepared by volume and the kinetics was followed at different temperatures to determine the activation parameters.

T a b l e - 100.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 743.6 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.0 mole litre^{-1}
10	6.0 "	0.993 " "
20	8.5 "	0.991 " "
40	13.0 "	0.986 " "
60	16.3 "	0.983 " "
80	19.7 "	0.979 " "
100	22.8 "	0.977 " "
120	25.8 "	0.974 " "
140	28.9 "	0.970 " "
160	32.8 "	0.967 " "

Rate constant = 3.2 x 10^{-6} litre $mole^{-1}sec^{-1}$
(Curve I, fig. 61)

Table - 101.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 743.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.0	mole	litre^{-1}
10	10.7	"	0.989	"	"
20	15.4	"	0.984	"	"
40	22.6	"	0.977	"	"
60	28.5	"	0.971	"	"
80	32.3	"	0.967	"	"
100	35.8	"	0.965	"	"
120	37.8	"	0.963	"	"
140	38.6	"	0.962	"	"
160	40.2	"	0.961	"	"

Rate constant = 5.55×10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 61)

Table - 102.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 748.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	6.0	ml	0.991	mole	litre^{-1}
10	15.0	"	0.984	"	"
20	25.3	"	0.975	"	"
40	32.8	"	0.967	"	"
60	39.5	"	0.961	"	"
80	46.8	"	0.954	"	"
100	51.2	"	0.951	"	"
120	56.2	"	0.944	"	"
140	61.8	"	0.939	"	"
160	67.3	"	0.934	"	"

Rate constant = 8.5×10^{-6} litre mole^{-1}sec^{-1}
(Curve III, fig. 61)

Table - 103.

Reaction bath temperature = 35 ± 0.1°C
Mean atmospheric pressure = 744.6 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	0.982 mole litre^{-1}
10	24.0 "	0.976 " "
20	30.0 "	0.971 " "
40	38.0 "	0.963 " "
60	43.8 "	0.958 " "
80	50.5 "	0.951 " "
100	55.2 "	0.946 " "
120	60.3 "	0.941 " "
140	65.4 "	0.936 " "
160	70.0 "	0.931 " "

Rate constant = 12.6 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve IV, fig. 61)

The activation parameters calculated as before are as follows:

E = 13.8 K cals mole^{-1}

$\Delta E^{\neq}$ = 13.0 K cals mole^{-1}

$\Delta F^{\neq}$ = 24.8 K cals mole^{-1}

$\Delta S^{\neq}$ = -39 e.u.

The activation parameters for acetic acid - thionyl chloride reaction in different systems can be summarised as below:

Table - 104.

	Xylene	Xylene(75%)— dioxane (25%)	Xylene(50%)— dioxane (50%)	Xylene(25%) - dioxane (75%)
Activation energy (E)	12.2 K_1 cals $mole^{-1}$	12.8K cals $mole^{-1}$	13.42K cals $mole^{-1}$	13.8K cals $mole^{-1}$
Frequency factor (A)	16.8 x 10^2 sec^{-1}	28 x 10^2 sec^{-1}	61.8 x 10^2 sec^{-1}	-
Internal energy of activation (at 303°K ($\Delta E^{\neq}$)	11.58K cals $mole^{-1}$	12.22K cals $mole^{-1}$	12.8K cals $mole^{-1}$	13.0 K cals $mole^{-1}$
Free energy of activation (at 303°K) ($\Delta F^{\neq}$)	23.98K cals $mole^{-1}$	24.42K cals $mole^{-1}$	24.71K cals $mole^{-1}$	24.8 K cals $mole^{-1}$
Entropy of activation (at 303°K) ($\Delta S^{\neq}$)	-42.3 e.u.	-40.3 e.u.	-39.2 e.u.	-39. e.u.

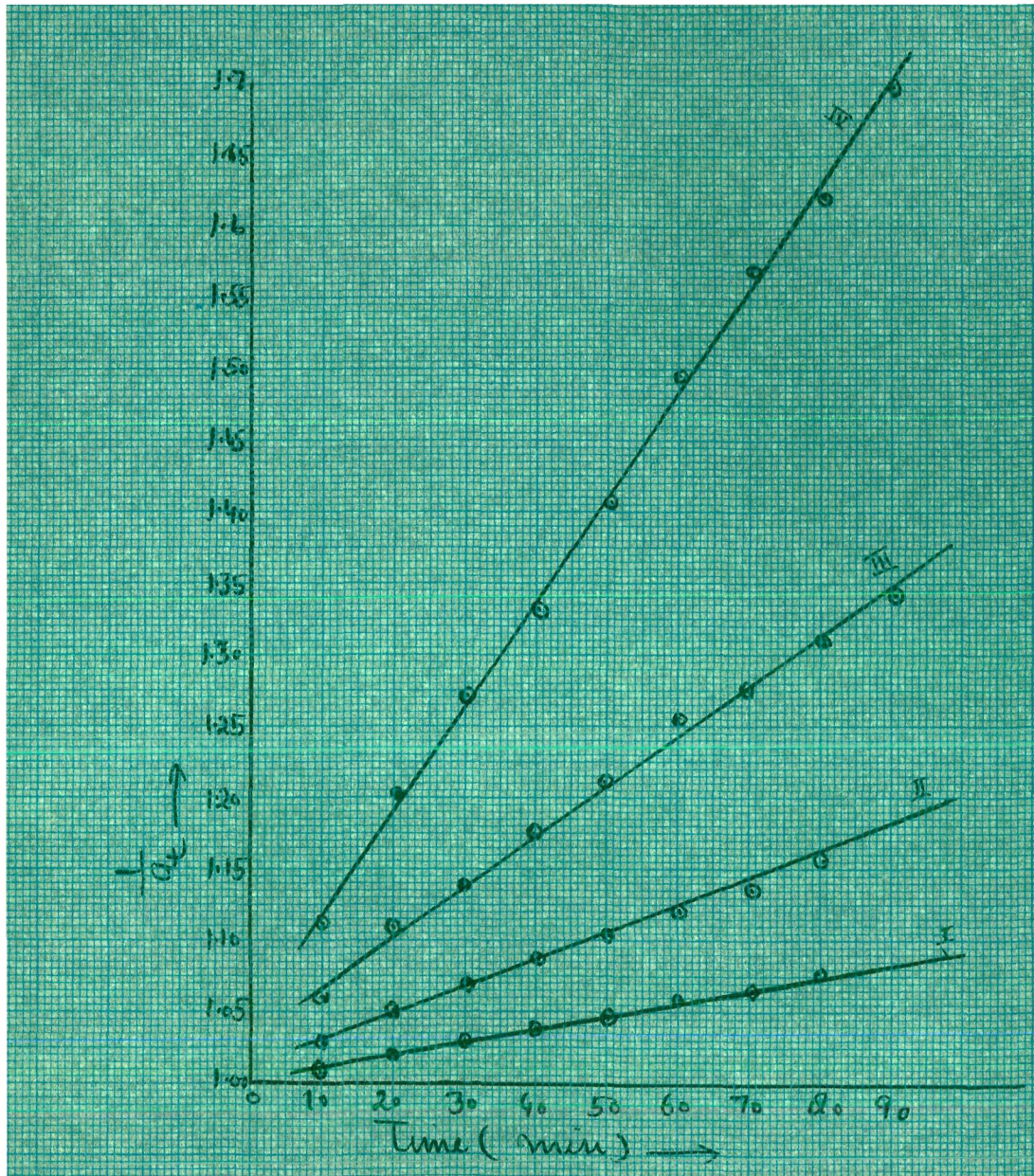


Fig. No. 63

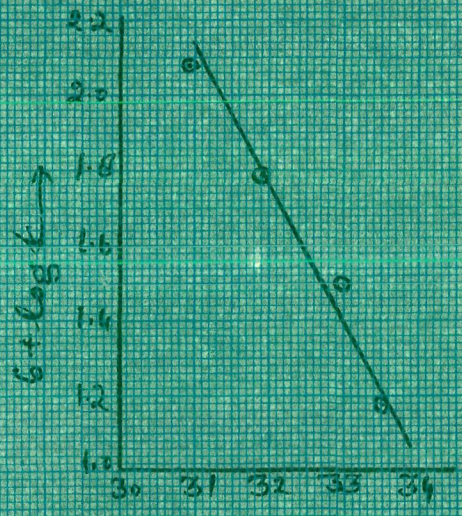


Fig. No. 64

Propionic Acid - thionyl chloride reaction

This reaction was also carried out in xylene and xylene-dioxane mixture of different compositions by volume. The thermodynamic functions were calculated as before. The results are recorded in the following tables.

Studies in Xylene

Table - 105.

Reaction bath temperature = $20 \pm 0.1^{o}C$
Mean atmospheric pressure = 743.5 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole litre^{-1}	
10	13.0	"	0.987	"	"
20	20.7	"	0.979	"	"
30	28.0	"	0.972	"	"
40	36.6	"	0.963	"	"
50	45.0	"	0.955	"	"
60	54.0	"	0.946	"	"
70	61.1	"	0.939	"	"
80	70.0	"	0.929	"	"
90	78.8	"	0.921	"	"

Rate constant = 15.2×10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 63)

Table - 106.

Reaction bath temperature = 30 ±,0.1°C
Mean atmospheric pressure = 742.7 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	30.8	"	0.963	" "
20	49.0	"	0.952	" "
30	66.0	"	0.935	" "
40	82.6	"	0.918	" "
50	94.0	"	0.908	" "
60	111.0	"	0.892	" "
70	123.0	"	0.880	" "
80	134.2	"	0.869	" "
90	145.1	"	0.858	" "

Rate constant = 28.3 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 63)

Table - 107.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 744.0 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	64.0	"	0.939	" "
20	90.2	"	0.908	" "
30	125.6	"	0.878	" "
40	155.2	"	0.851	" "
50	180.1	"	0.826	" "
60	192.3	"	0.812	" "
70	208.3	"	0.784	" "
80	225.4	"	0.766	" "
90	252.8	"	0.742	" "

Rate constant = 61.3 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve III, fig. 63)

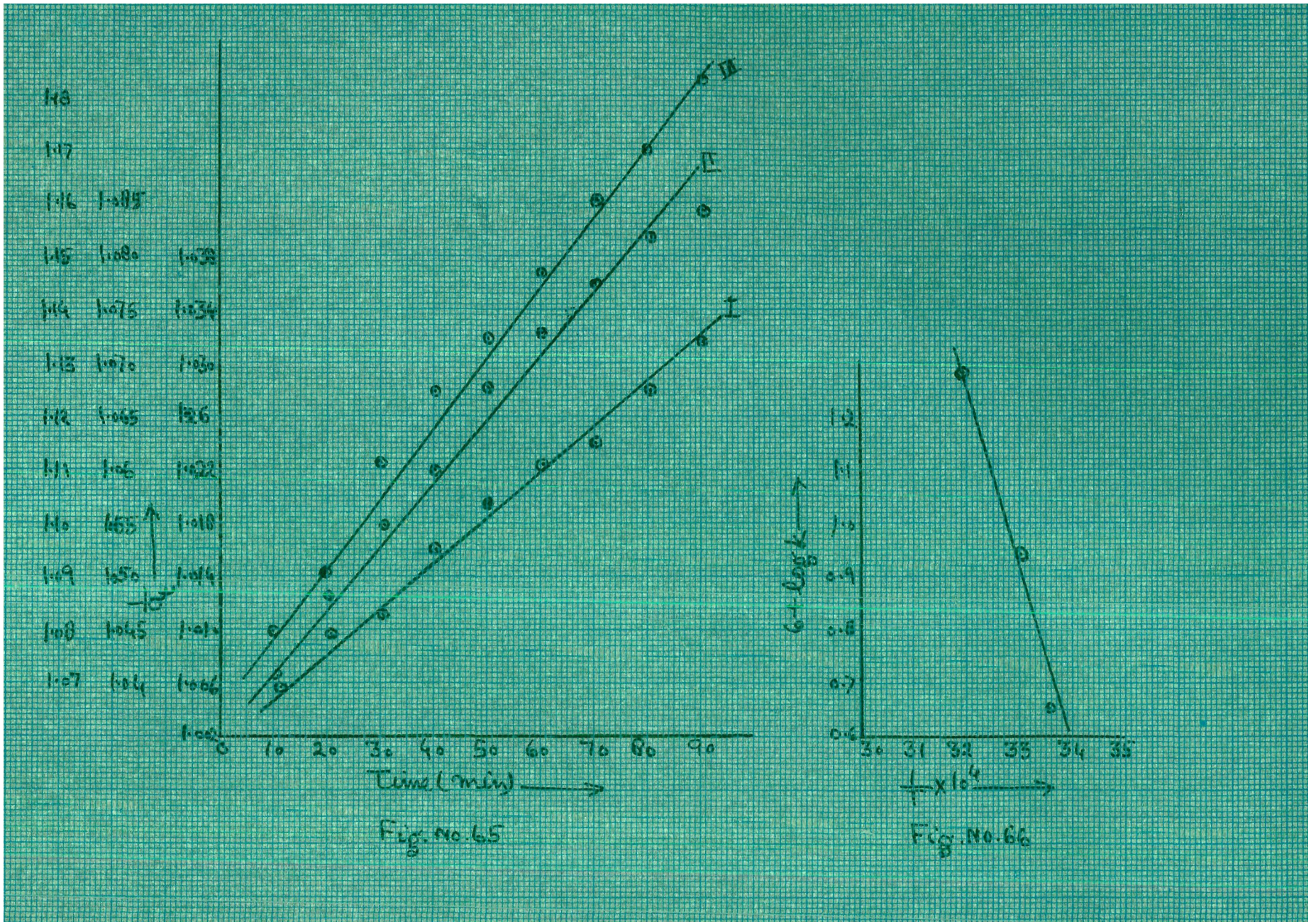


Fig. No. 65

Fig. No. 66

Table - 108.

Reaction bath temperature = 50 ± 0.1°C
Mean atmospheric pressure = 748.5 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	132.5 "	0.876 " "
20	194.1 "	0.819 " "
30	252.2 "	0.764 " "
40	299.7 "	0.720 " "
50	339.6 "	0.683 " "
60	372.0 "	0.653 " "
70	400.0 "	0.630 " "
80	423.4 "	0.605 " "
90	440.5 "	0.589 " "

Rate constant = 123.4 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve IV, fig. 63)

Studies in xylene (75%) — dioxane (25%) mixture

Table - 109.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 743.0 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	6.3 "	0.993 " "
20	12.2 "	0.987 " "
30	15.3 "	0.984 " "
40	17.5 "	0.982 " "
50	19.8 "	0.979 " "
60	22.3 "	0.977 " "
70	24.2 "	0.975 " "
80	26.8 "	0.972 " "
90	29.0 "	0.970 " "

Rate constant = 4.5 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 65)

Table - 110.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 742.5 mm
Reaction mixture: 10 ml each CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
10	43.5	"	0.957	" "
20	48.0	"	0.952	" "
30	55.6	"	0.947	" "
40	59.9	"	0.942	" "
50	67.1	"	0.936	" "
60	71.6	"	0.931	" "
70	75.2	"	0.928	" "
80	78.1	"	0.925	" "
90	80.0	"	0.920	" "

Rate constant = 8.77 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 65)

Table - 111.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 745.0 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
1	32.0	ml	0.971	mole litre^{-1}
10	80.0	"	0.926	" "
20	86.7	"	0.920	" "
30	103.3	"	0.904	" "
40	118.8	"	0.890	" "
50	127.5	"	0.882	" "
60	136.4	"	0.873	" "
70	147.0	"	0.864	" "
80	158.0	"	0.855	" "
90	165.6	"	0.846	" "

Rate constant = 19.1 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve III, fig. 65)

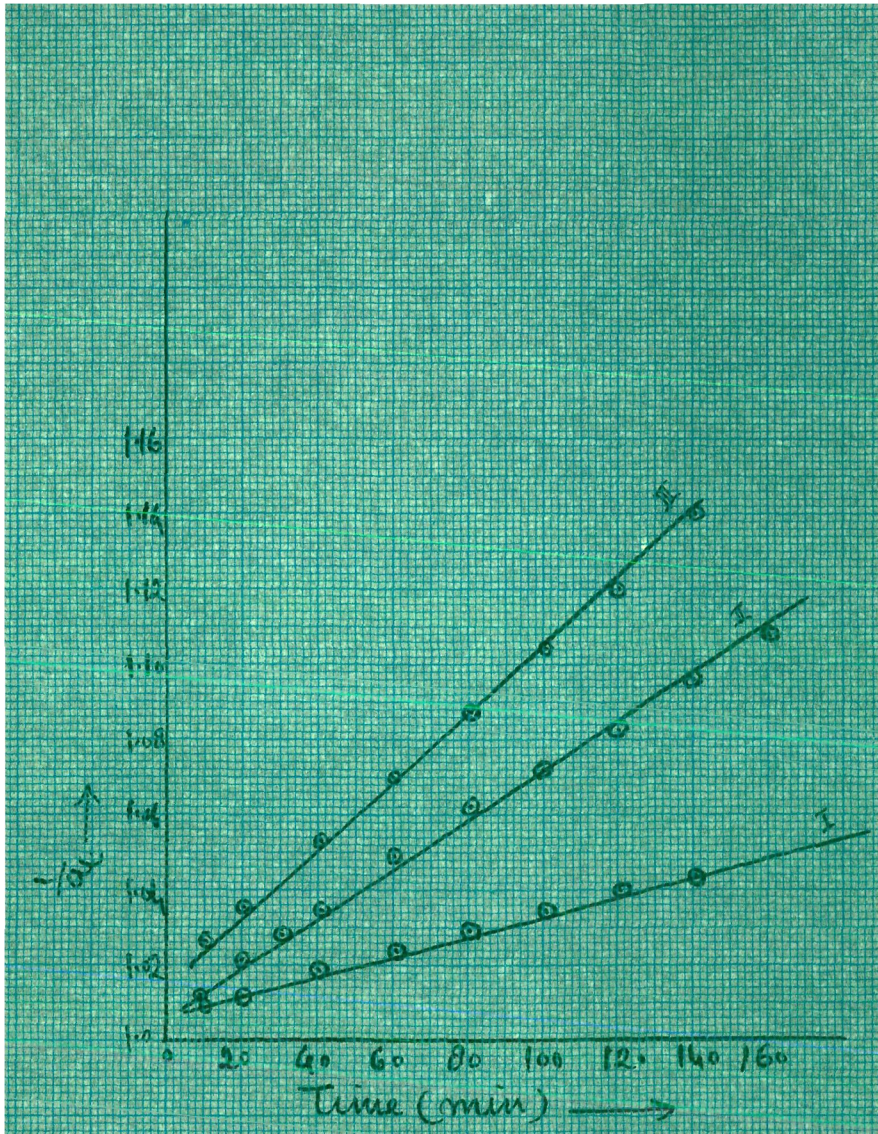


Fig. No. 47

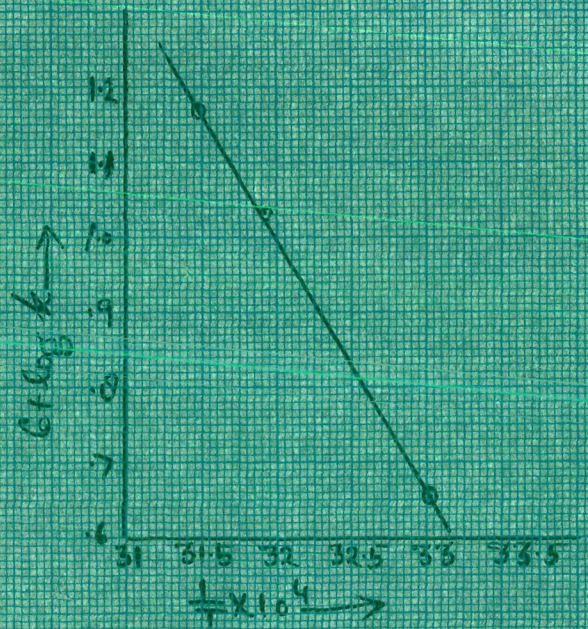


Fig. No. 48

Studies in xylene (50%) —— dioxane (50%) mixture

Table - 112.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 744.0 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.0	mole litre^{-1}	
10	16.2	"	0.984	"	"
20	22.2	"	0.978	"	"
40	29.3	"	0.971	"	"
60	36.1	"	0.964	"	"
80	42.0	"	0.959	"	"
100	48.1	"	0.952	"	"
120	54.2	"	0.946	"	"
140	59.2	"	0.941	"	"
160	65.0	"	0.935	"	"

Rate constant = 5.8×10^{-6} litre mole^{-1}sec^{-1}
(Curve I, fig. 67)

Table - 113.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 744.0 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole litre^{-1}	
10	28.2	"	0.973	"	"
20	42.2	"	0.957	"	"
30	47.4	"	0.954	"	"
40	54.4	"	0.948	"	"
50	62.9	"	0.935	"	"
60	70.1	"	0.930	"	"
70	76.5	"	0.927	"	"
80	82.8	"	0.922	"	"
90	87.3	"	0.916	"	"

Rate constant = 12.8×10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 67)

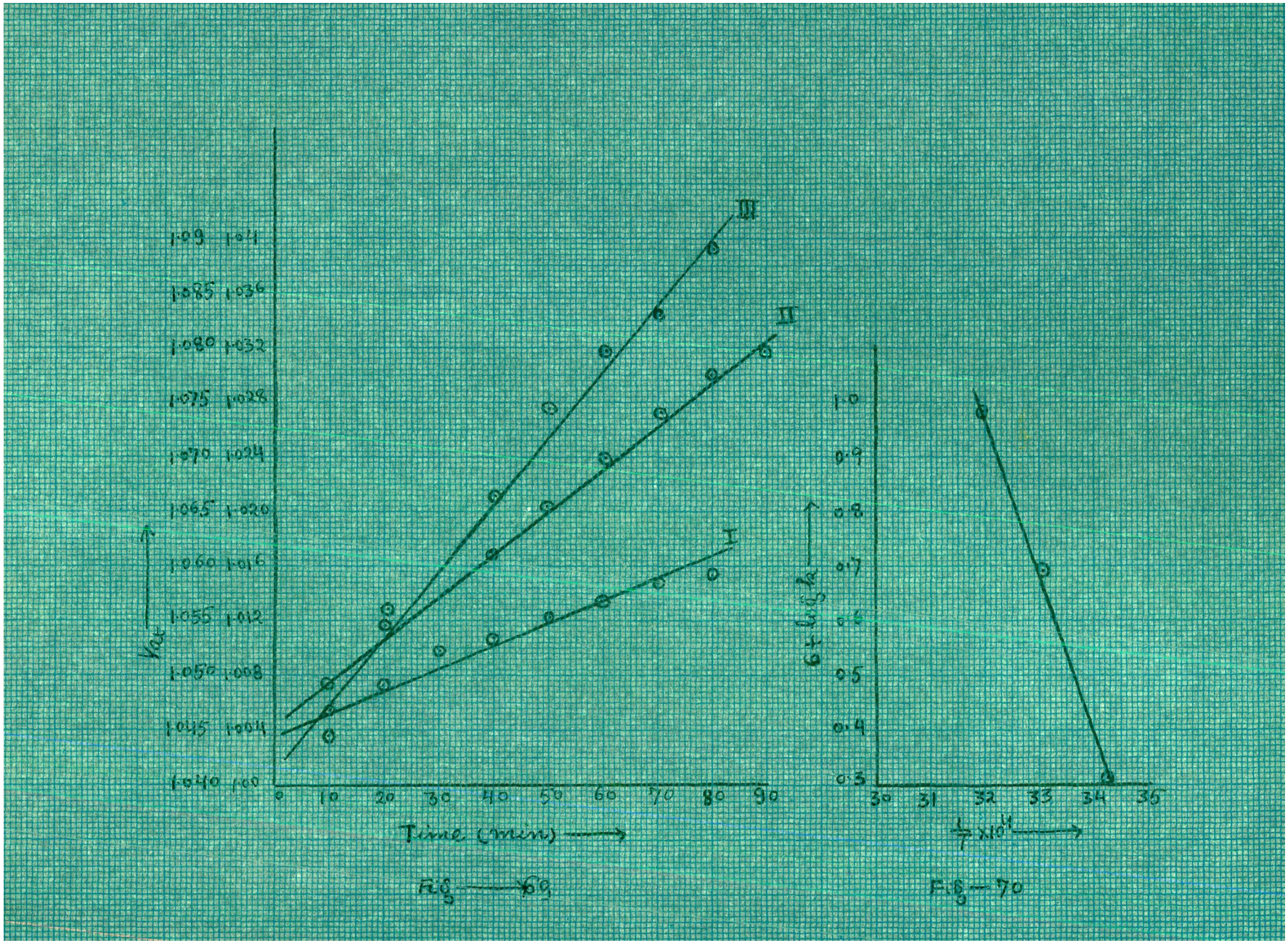

1·09 1·044
1·085 1·036
1·080 1·032
1·075 1·028
1·070 1·024
1·065 1·020
1·060 1·016
1·055 1·012
1·050 1·008
1·045 1·004
1·040 1·00
Vol
III
II
I
0 10 20 30 40 50 60 70 80 90
Time (min) ⟶
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
30 31 32 33 34 35
$\frac{1}{T} \times 10^{4}$ ⟶

Fig — 69

Fig — 70

Table - 114.

Reaction bath temperature = 50 ± 0.1°C
Mean atmospheric pressure = 746.5 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	12.0 ml	0.988 mole litre^{-1}
10	53.3 "	0.950 " "
20	65.1 "	0.939 " "
30	77.0 "	0.928 " "
40	90.1 "	0.917 " "
50	100.2 "	0.906 " "
60	111.6 "	0.895 " "
70	123.4 "	0.884 " "
80	134.0 "	0.974 " "

Rate constant = 22.4 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve III, fig. 67)

Studies in xylene (25%) —— dioxane (75%) mixture

Table - 115.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 743.6 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	6.2 "	0.9946 " "
20	8.4 "	0.9926 " "
40	11.4 "	0.9900 " "
60	13.6 "	0.9881 " "
80	16.6 "	0.9854 " "
100	19.5 "	0.9829 " "
120	22.3 "	0.9804 " "
140	25.0 "	0.9780 " "
160	27.7 "	0.9757 " "

Rate constant = 2.1 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve I, fig. 69)

Table - 116.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 743.6 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
1	6.2	ml	0.994	mole litre^{-1}
10	18.0	"	0.981	" "
20	22.9	"	0.978	" "
40	28.5	"	0.971	" "
60	32.9	"	0.967	" "
80	35.9	"	0.962	" "
100	41.2	"	0.957	" "
120	46.3	"	0.952	" "
140	50.3	"	0.948	" "
160	54.1	"	0.942	" "

Rate constant = 4.96 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 69)

Table - 117.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 744.0 mm
Reaction mixture: 10 ml each 2M CH_3CH_2COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
1	8.8	ml	0.991	mole litre^{-1}
10	46.0	"	0.954	" "
20	57.7	"	0.946	" "
30	65.3	"	0.937	" "
40	74.5	"	0.931	" "
50	81.3	"	0.923	" "
60	87.3	"	0.916	" "
70	91.8	"	0.918	" "
80	95.4	"	0.911	" "

Rate constant = 9.8 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve III, fig. 69)

Table - 118.

The thermodynamic factors for propionic acid-thionyl chloride reaction in solvents of different compositions.

	Xylene	Xylene (75%) — dioxane (25%) mixture	Xylene (50%) — dioxane (50%) mixture	Xylene (25%) — dioxane (75%)
Activation energy (E)	12.36K cals $mole^{-1}$	13.7K cals $mole^{-1}$	14.6K cals $mole^{-1}$	15.1K cals $mole^{-1}$
Frequency factor (A)	22.4×10^2 sec^{-1}	50×10^3 sec^{-1}	15.1×10^4 sec^{-1}	19.9×10^4 sec^{-1}
Internal energy of activation (at 303°K) ($\Delta E^{\ddagger}$)	12.8K cals $mole^{-1}$	13.1K cals $mole^{-1}$	14.05K cals $mole^{-1}$	14.6K cals $mole^{-1}$
Free energy of activation (at 303°K) ($\Delta F^{\ddagger}$)	24.1K cals $mole^{-1}$	24.8K cals $mole^{-1}$	25.0K cals $mole^{-1}$	25.2K cals $mole^{-1}$
Entropy of activation (at 303°K) ($\Delta S^{\ddagger}$)	-40.7 e.u.	-37.0 e.u.	-36.1 e.u.	-35.0 e.u.

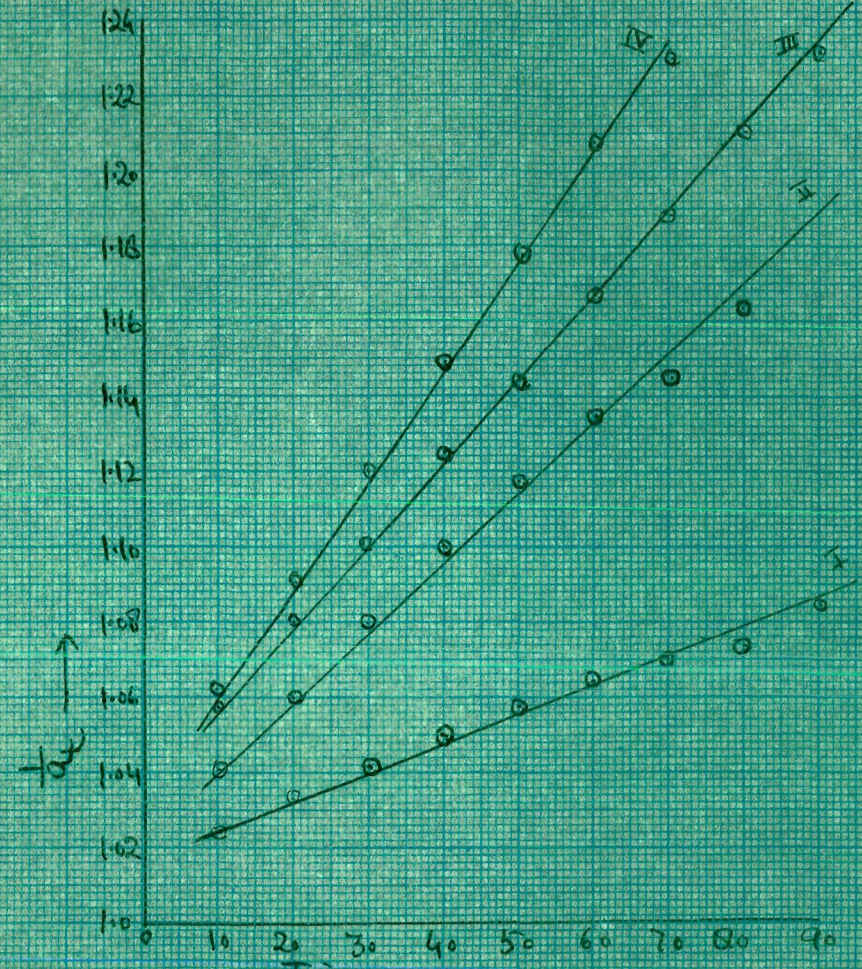


Fig NO 71

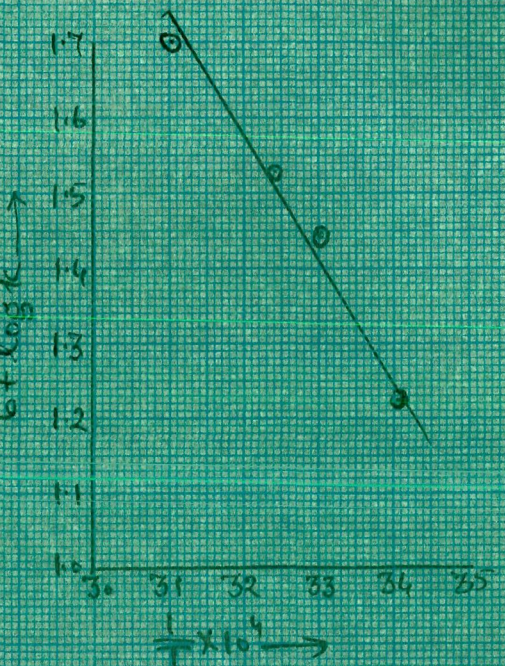


Fig NO 72

Studies with Butyric Acid

Similar investigationswere also carried out with butyric acid. The rate constants and other thermodynamic functions were determined as before. The following are the results.

Studies in Xylene

Table - 119.

Reaction bath temperature = $20 \pm 0.1^{\circ}C$
Mean atmospheric pressure = 746.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	11.3 ml	0.99 mole litre^{-1}
10	22.7 "	0.977 " "
20	34.2 "	0.966 " "
30	40.8 "	0.959 " "
40	48.4 "	0.952 " "
50	55.0 "	0.945 " "
60	61.5 "	0.939 " "
70	68.0 "	0.932 " "
80	73.1 "	0.927 " "
90	79.0 "	0.921 " "

Rate constant = 13.2×10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 71)

Table - 120.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 746.4 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
3	24.3 ml	0.976 mole litre^{-1}
10	47.8 "	0.951 " "
20	56.4 "	0.944 " "
30	75.1 "	0.925 " "
40	91.4 "	0.909 " "
50	106.4 "	0.894 " "
60	120.0 "	0.880 " "
70	132.2 "	0.873 " "
80	141.6 "	0.859 " "
90	152.2 "	0.846 " "

Rate constant = 30.1 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 71)

Table - 121.

Reaction bath temperature =35 ± 0.1°C
Mean atmospheric pressure = 749.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	13.2 ml	0.984 mole litre^{-1}
10	54.5 "	0.944 " "
20	76.1 "	0.925 " "
30	93.0 "	0.907 " "
40	111.5 "	0.889 " "
50	128.0 "	0.873 " "
60	144.0 "	0.857 " "
70	158.2 "	0.842 " "
80	176.0 "	0.826 " "
90	190.7 "	0.812 " "

Rate constant = 35.7 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 71)

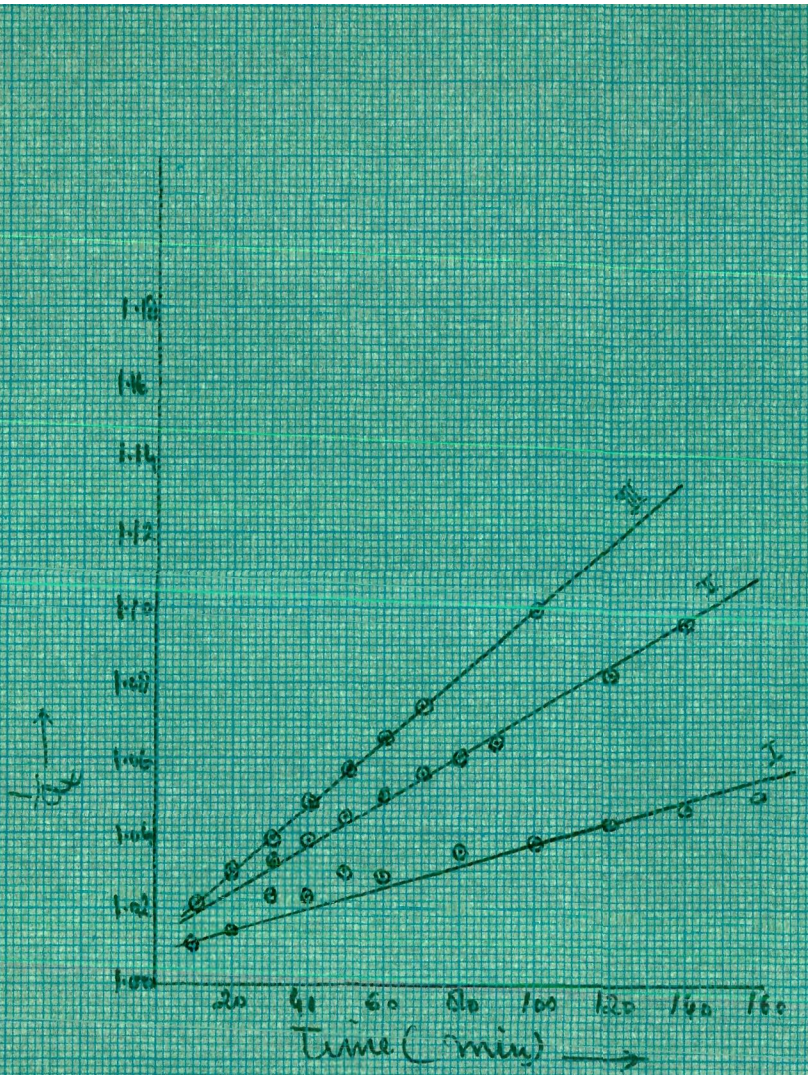


Fig No 73

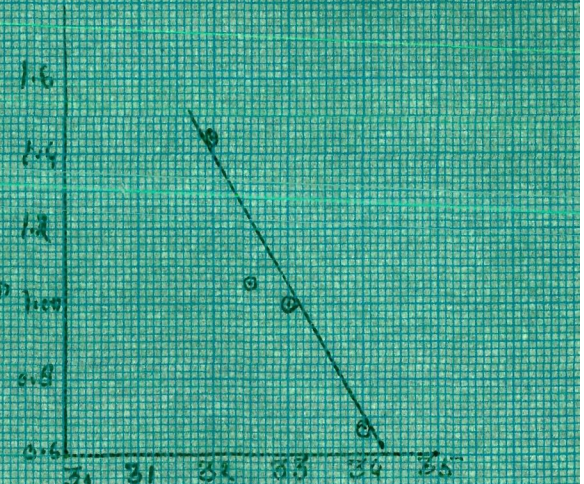


Fig No 74

Table - 122.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 748.5 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	14.1 ml	0.986 mole litre^{-1}
10	56.8 "	0.943 " "
20	83.6 "	0.917 " "
30	108.6 "	0.892 " "
40	131.0 "	0.870 " "
50	152.0 "	0.849 " "
60	171.0 "	0.828 " "
70	189.6 "	0.808 " "

Rate constant = 50 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve IV, fig. 71)

Studies In Xylene (75%) — dioxane (25%) mixtures

Table - 123.

Reaction bath temperature = 20 ± 0.1°C
Mean atmospheric pressure = 749.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
10	9.0 "	0.992 " "
20	16.4 "	0.986 " "
40	25.9 "	0.974 " "
60	32.0 "	0.971 " "
80	37.5 "	0.962 " "
100	39.6 "	0.961 " "
120	42.8 "	0.958 " "
140	44.7 "	0.956 " "
160	48.1 "	0.953 " "

Rate constant = 4.66 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 73)

Table - 124.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 745.6 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	6.0 ml	0.994 mole litre^{-1}
10	18.4 "	0.981 " "
20	24.0 "	0.976 " "
30	29.6 "	0.970 " "
40	34.5 "	0.966 " "
50	42.3 "	0.958 " "
60	46.7 "	0.953 " "
70	52.6 "	0.942 " "
80	58.6 "	0.947 " "
90	60.5 "	0.942 " "
120	75.8 "	0.924 " "

Rate constant = 9.64 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 73)

Table - 125.

Reaction bath temperature = 35 ± 0.1°C
Mean atmospheric pressure = 745.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_3COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	6.2 ml	0.994 mole litre^{-1}
10	20.6 "	0.979 " "
20	30.0 "	0.970 " "
30	38.4 "	0.962 " "
40	46.1 "	0.954 " "
50	53.8 "	0.946 " "
60	61.3 "	0.940 " "
70	68.0 "	0.933 " "
80	75.0 "	0.926 " "
90	81.2 "	0.921 " "

Rate constant = 14.3 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve III, fig. 73)

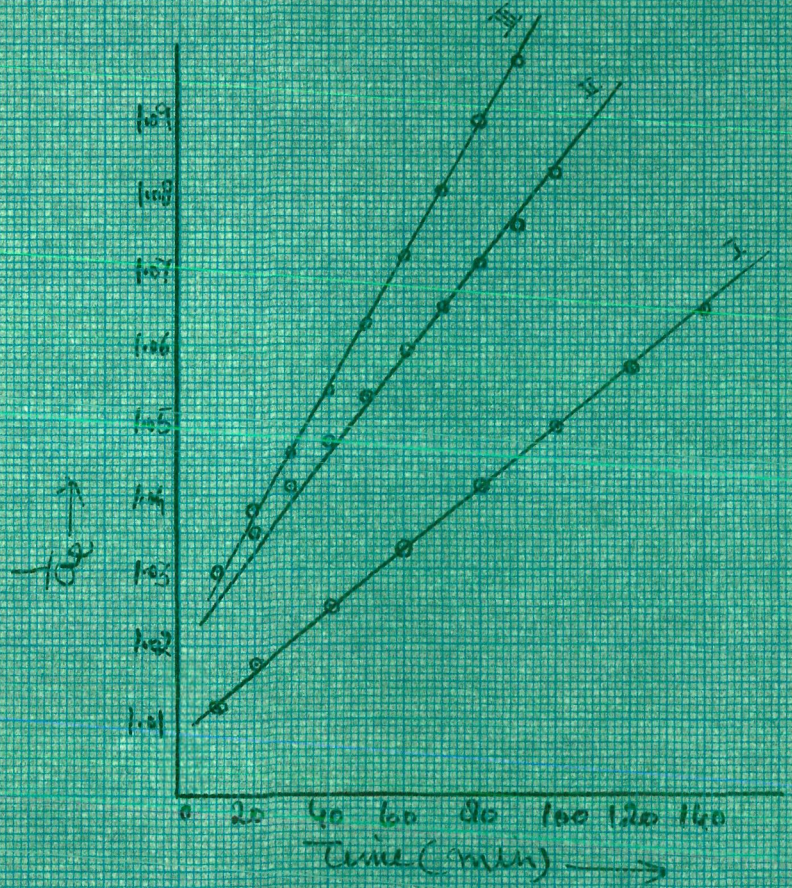


Fig. No. 75

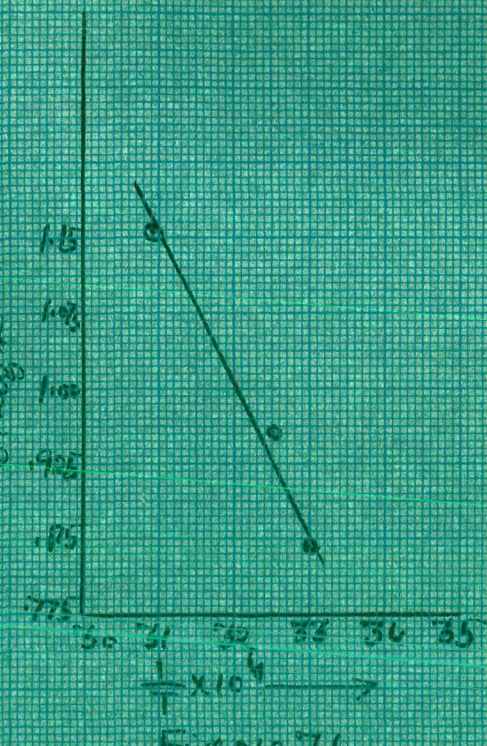


Fig. No 76

Table - 126.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 747.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
1	9.0	ml	0.992	mole litre^{-1}
10	39.0	"	0.961	" "
20	56.7	"	0.944	" "
30	71.0	"	0.929	" "
40	84.3	"	0.916	" "
50	98.1	"	0.902	" "
60	105.3	"	0.890	" "
70	114.3	"	0.886	" "
80	123.3	"	0.877	" "
90	131.3	"	0.870	" "

Rate constant = 29.6 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve IV, fig. 73)

Studies in xylene (60%) — dioxane (40%) mixture

Table - 127.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 743.7 mm
Reaction mixture: 10 ml each $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
1	4.1	ml	0.996	mole litre^{-1}
10	12.2	"	0.988	" "
20	17.2	"	0.983	" "
30	21.5	"	0.979	" "
40	25.0	"	0.975	" "
50	29.0	"	0.972	" "
60	32.9	"	0.968	" "
80	39.9	"	0.961	" "
100	48.0	"	0.953	" "
120	54.8	"	0.946	" "
140	61.5	"	0.939	" "

Rate constant = 7 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve I, fig. 75).

Table - 128.

Reaction bath temperature = 35 ± 0.1°C
Mean atmospheric pressure = 745.7 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	5.8 ml	0.994 mole litre^{-1}
10	14.7 "	0.985 " "
20	30.5 "	0.970 " "
30	41.5 "	0.959 " "
40	46.7 "	0.954 " "
50	52.0 "	0.948 " "
60	57.1 "	0.943 " "
70	61.5 "	0.939 " "
80	66.9 "	0.933 " "
90	73.0 "	0.928 " "
100	78.5 "	0.922 " "
110	83.3 "	0.917 " "
120	88.8 "	0.912 " "

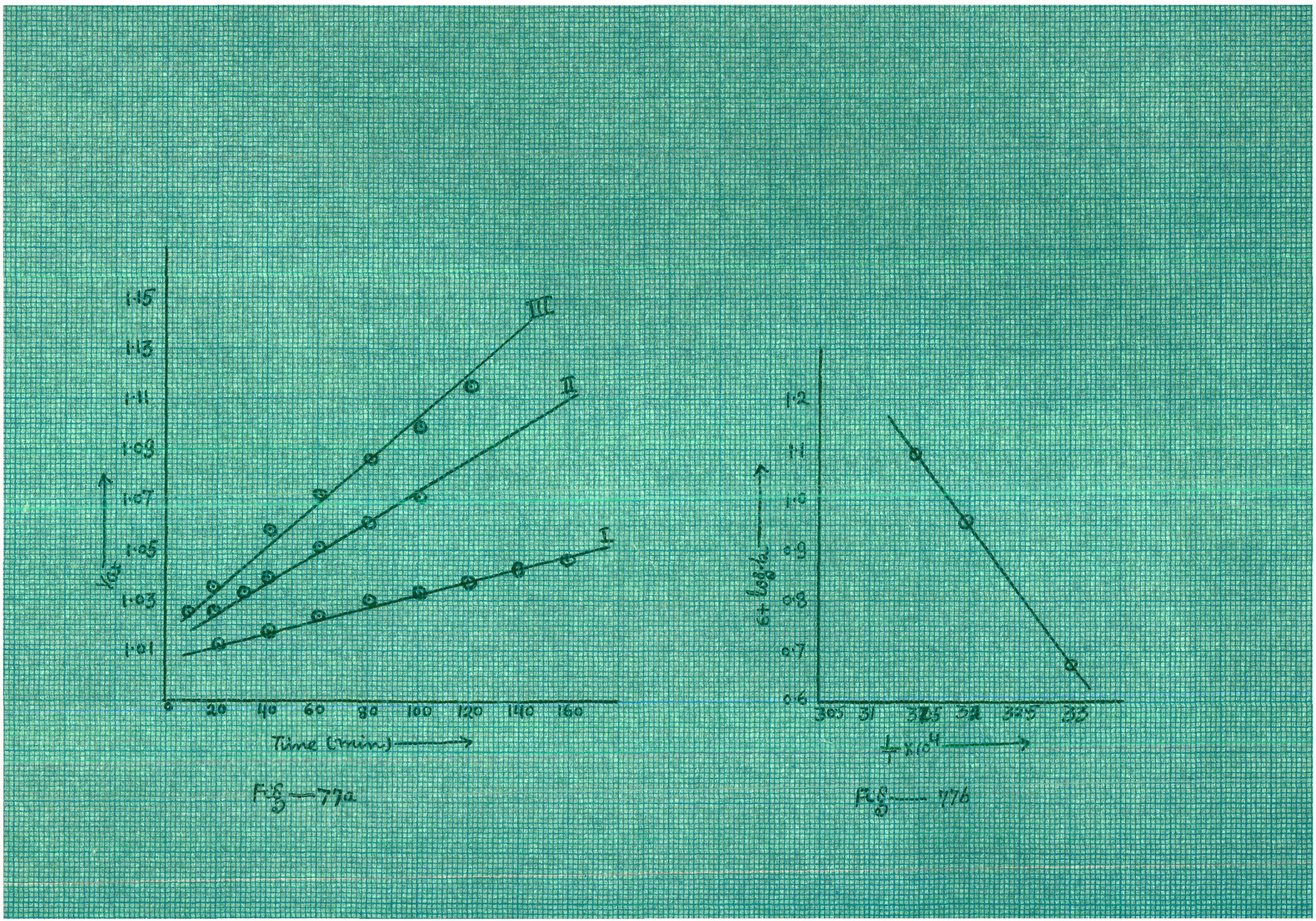
Rate constant = 10.6 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve II, fig. 75)

Table - 129.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 746.5 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
1	6.8 ml	0.993 mole litre^{-1}
10	28.8 "	0.972 " "
20	36.9 "	0.962 " "
30	44.9 "	0.956 " "
40	52.7 "	0.948 " "
50	60.7 "	0.940 " "
60	68.5 "	0.932 " "
70	75.7 "	0.925 " "
80	82.7 "	0.918 " "
90	89.6 "	0.911 " "

Rate constant = 14.5 x 10^{-6} litre mole^{-1}sec^{-1}
(Curve III, fig. 75)


1·15
1·13
1·11
1·09
1·07
1·05
1·03
1·01
log θ/θ₀
III
II
I
0
20
40
60
80
100
120
140
160
Time (min) ⟶

Fig—7a

1·2
1·1
1·0
0·9
0·8
0·7
0·6
log θ/θ₀
30·5
31
31·5
32
32·5
33
1/T x 10⁴ ⟶

Fig—7b

Studies in xylene (50%) — dioxane (50%) mixture

Table - 130.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 748.5 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	litre^{-1}
10	9.2	"	0.991	"	"
20	12.2	"	0.988	"	"
40	18.7	"	0.981	"	"
60	24.2	"	0.976	"	"
80	29.0	"	0.971	"	"
100	33.8	"	0.966	"	"
120	37.4	"	0.963	"	"
140	42.0	"	0.958	"	"
160	46.2	"	0.953	"	"

Rate constant = 4.54×10^{-6} litre mole^{-1} sec^{-1}
(Curve I, fig. 77)

Table - 131.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 746.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
1	3.6	ml	0.997	mole	litre^{-1}
10	19.6	"	0.901	"	"
20	27.4	"	0.974	"	"
30	34.6	"	0.967	"	"
40	41.0	"	0.961	"	"
60	48.0	"	0.949	"	"
80	58.4	"	0.944	"	"
100	68.4	"	0.934	"	"
120	78.4	"	0.924	"	"
140	88.0	"	0. 913	"	"
160	98.1	"	0.902	"	"

Rate constant = 11×10^{-6} litre mole^{-1} sec^{-1}
(Curve II, fig. 77)

Table - 132.

Reaction bath temperature = 45 ± 0.1°C
Mean atmospheric pressure = 746.0 mm
Reaction mixture: 10 ml each 2M $CH_3(CH_2)_2COOH$ & 2M $SOCl_2$

Time (Min)	Vol. of gas evolved	Concentration of the reactants
1	4.2 ml	0.996 mole litre^{-1}
10	25.8 "	0.974 " "
20	34.6 "	0.965 " "
40	57.5 "	0.942 " "
60	65.3 "	0.935 " "
80	79.7 "	0.920 " "
100	93.7 "	0.906 " "
120	106.8 "	0.893 " "
140	114.5 "	0.885 " "

Rate constant = 15 x 10^{-6} litre mole^{-1} sec^{-1}
(Curve III, fig. 77)

The rate constants were evaluated from the slopes of $\frac{1}{at}$ versus time plots. The activation energies for all the systems were calculated from the slopes of log k versus $\frac{1}{T}$ curves (vide figures 72, 74, 76, 78). The activation parameters were calculated as described previously. The results are given in the following table.

Table - 133.

Thermodynamic factors for butyric acid - thionyl chloride reaction in different solvents.

	Xylene	Xylene (75%) — dioxane (25%)	Xylene (50%) — dioxane (50%)	Xylene (25%) — dioxane (75%)
Activation energy (E)	11.5K cals $mole^{-1}$	13.2K cals $mole^{-1}$	14.2K cals $mole^{-1}$	17.4K cals $mole^{-1}$
Frequency factor (A)	5.7×10^3 sec^{-1}	14.8×10^3 sec^{-1}	7.0×10^4 sec^{-1}	14.1×10^5 sec^{-1}
Internal energy of activation (at 303°K) ($\Delta E^{\neq}$)	11.44K cals $mole^{-1}$	13.1K cals $mole^{-1}$	14.13K cals $mole^{-1}$	17.3K cals $mole^{-1}$
Free energy of activation (at 303°K) ($\Delta F^{\neq}$)	23 K cals $mole^{-1}$	23.8K cals $mole^{-1}$	23.9K cals $mole^{-1}$	23.6K cals $mole^{-1}$
Entropy of Activation (at 303°K) ($\Delta S^{\neq}$)	-38.3 e.u.	-35.1 e.u.	-32.0 e.u.	-20.5 e.u.

C H A P T E R - V

INFLUENCE OF REACTION PRODUCTS ON RATE

While studying fatty acid - thionyl chloride reaction (described earlier), it was observed that it follows second order kinetics only in the beginning and the reaction shows strong autoinhibition afterwards. The data, obtained after about 36% of the reaction was over, did not fit in to any simple kinetic equation. This autoinhibition has however been explained by studying the reaction in presence of the reaction products added from outside in the reaction mixture.

A survey of literature on fatty acids - thionyl chloride system, as made earlier, shows that the poor yield that has always been the problem has remained unexplained.

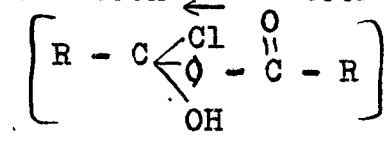
According to Goggins[112] the formation of acid chloride from the interaction of acid and acid-chloride proceeds through the intermediate formation of anhydride

$$R\,COCl + R'\,COOH \rightleftharpoons RCO.OCOR + HCl \rightleftharpoons R\,COOH + R'\,COCl$$

He therefore recommended that acid anhydride can be

prepared by refluxing equimolar mixture of an acid and acid chloride or by removing the hydrogen chloride by other means, such as an added base like pyridine[113]. This however, does not usually yield anhydride in appreciable amount, therefore, Brown postulated that the formation of acid chloride from the interaction of an acid and acid chloride takes place directly as

$$R\ COCl + R'\ COOH \rightleftharpoons R\ COOH + R'\ COCl$$ or indirectly through



According to Brown[114] the formation of both anhydride and chloride may take place through the same intermediate.

Howold[115] studies the solvolysis of acetyl chloride in glacial acetic acid and reported the following reaction

$$CH_3\ COCl + CH_3\ COOH \rightleftharpoons (CH_3CO)_2O + HCl$$

The foregoing references on acid and acid chloride reaction is lead us to think that the auto-inhibition referred earlier and the poor yield of acid chloride may be due to the occurrence of a side reaction between the acid and its chloride.

With this view, the influence of acetyl chloride, acetic anhydride and dioxane on the reaction was studied

in detail. The presence of acetic anhydride or acetyl chloride in the reaction mixture suppressed the evolution of gases. To know whether this evolution of the two gases is suppressed equally, the gases were dissolved in water and chloride ion was determined potentiometrically using Ag - AgCl electrode in conjunction with calomel electrode. The volume of HCl in the gas mixture was calculated from the chloride concentration.

E X P E R I M E N T A L

The reagents acetic acid and thionyl chloride and the solvents chlorobenzene, bromobenzene, nitrobenzene and xylene were B.D.H. laboratory grade and were purified as before. Acetyl chloride (E. Merck) and acetic anhydride (B.D.H.) were purified as follows.

Acetyl Chloride[116]

Acetyl chloride was distilled in an all glass assembly. The fraction between 51 - 52°C was collected in a receiver which had anhydrous calcium chloride tube in its side arm. It was stored in coloured bottle.

Purification of Acetic anhydride[117]

Commercial acetic anhydride (B.D.H.) was fractionated through a glass bead coloumn until it gave fairly a constant boiling point and was relatively free from lower boiling acids. It was then refractionated twice over fused sodium salt of the corresponding fatty acid and twice under reduced pressure. The constancy of the density as recommended by Timmermans and Hennaut-Roland[118] was taken as the criteria of purity.

Effect of Acetic Anhydride

The influence of acetic anhydride on acetic acid-thionyl chloride reaction was studied by following the kinetics in nitrobenzene in presence of different amounts of acetic anhydride added from outside. The reaction was followed as before. The results obtained with and without acetic anhydride are given in the following tables.

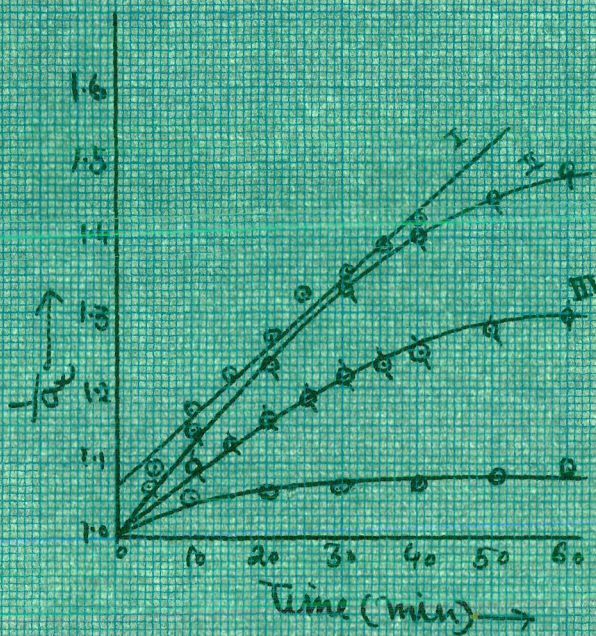


Fig No. 28

Table - 134.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 744.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$
(4 ml nitrobenzene was added to the reaction mixture)

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
5	97.8 "	0.906 " "
10	148.0 "	0.858 " "
15	191.0 "	0.817 " "
20	225.4 "	0.784 " "
25	252.6 "	0.758 " "
30	275.8 "	0.736 " "
35	295.0 "	0.718 " "
40	309.0 "	0.704 " "
60	350.8 "	0.666 " "

R (Curve I, fig. 78)

Table - 135.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 745.2 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$
(1 cc acetic anhydride + 3 ml nitrobenzene were added in the reaction mixture)

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
5	73.0 "	0.928 " "
6	93.0 "	0.908 " "
8	112.0 "	0.889 " "
10	135.1 "	0.886 " "
15	178.5 "	0.823 " "
20	216.5 "	0.786 " "
25	241.1 "	0.761 " "
30	261.5 "	0.742 " "
40	307.0 "	0.696 " "
50	319.0 "	0.684 " "
60	330.5 "	0.667 " "

(Curve II, fig. 78)

Table - 136.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 746.3 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$
(1.5 ml acetic anhydride + 2.5 ml nitrobenzene were added in reaction mixture).

Time (Min.).	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
5	45.0	"	0.945	" "
10	80.6	"	0.920	" "
15	113.0	"	0.888	" "
20	140.8	"	0.861	" "
25	164.0	"	0.838	" "
30	181.0	"	0.820	" "
35	194.5	"	0.807	" "
40	204.5	"	0.798	" "
50	220.5	"	0.782	" "
60	230.5	"	0.770	" "

(Curve III, fig. 78)

Table - 137.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 743.8 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$
(4 ml of acetic anhydride was added in reaction mixture)

Time (Min.)	Vol. of gas evolved		Concentration of the reactants	
0	0	ml	1.00	mole litre^{-1}
5	28.0	"	0.975	" "
10	51.2	"	0.954	" "
15	61.2	"	0.945	" "
20	68.2	"	0.938	" "
25	73.2	"	0.934	" "
30	77.0	"	0.931	" "
40	82.7	"	0.926	" "
50	86.9	"	0.922	" "
60	91.6	"	0.918	" "
70	94.7	"	0.915	" "
80	98.0	"	0.912	" "
90	100.7	"	0.909	" "
100	103.6	"	0.907	" "
110	106.8	"	0.904	" "
120	108.2	"	0.902	" "

(Curve IV, fig. 78)

Effect of dioxane

Influence of dioxane on reaction rate was seen by adding one cc of dioxane in reaction mixture, prepared in nitrobenzene. The kinetics was followed as described earlier.

Table - 138.

Volume of gas (HCl & SO_2) evolved from 10 ml each 2M solutions of acetic acid and thionyl chloride in nitrobenzene at 30°C and 742.3 mm pressure.

Time (Min.)	Medium saturated with HCl & SO_2	1 cc dioxane
5	97.8 ml	84.0 ml
10	148.2 "	125.0 "
15	191.0 "	158.0 "
20	225.0 "	185.5 "
25	275.0 "	204.0 "
30	294.0 "	221.5 "
40	-	239.0 "
50	331.0 "	250.0 "
60	348.0 "	269.0 "

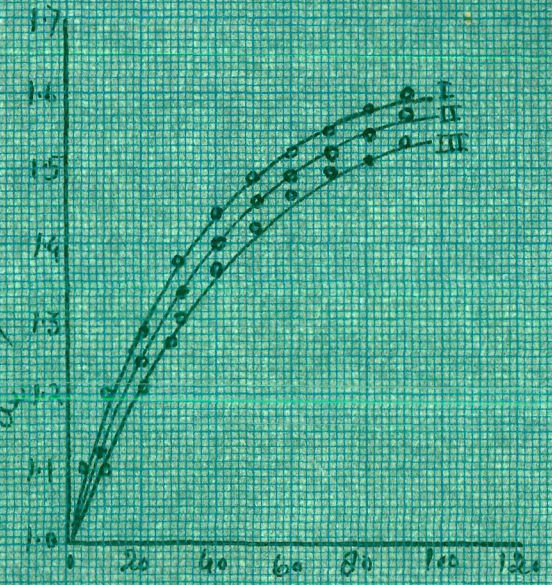


Fig. No- 79

Effect of Acetyl Chloride

Influence of acetyl chloride on this reaction was studied likewise. All the sets were studied in nitrobenzene at 30°C.

Table - 139.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 747.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$
(1 ml acetyl chloride was added in nitrobenzene)

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole litre^{-1}	
5	93.0	"	0.907	"	"
10	143.0	"	0.856	"	"
15	189.0	"	0.817	"	"
20	224.1	"	0.778	"	"
25	254.0	"	0.748	"	"
30	277.0	"	0.725	"	"
40	310.2	"	0.700	"	"
50	334.2	"	0.667	"	"
60	346.8	"	0.654	"	"
70	360.3	"	0.638	"	"
80	369.8	"	0.629	"	"
90	371.6	"	0.623	"	"

(Curve I, fig. 79)

Table - 140.

Reaction bath temperature = $30 \pm 0.1^{\circ}C$
Mean atmospheric pressure = 749.3 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

(3 ml acetyl chloride was added in nitrobenzene)

Time (Min.)	Vol. of gas evolved		Concentration of the reactants		
0	0	ml	1.00	mole	Litre^{-1}
5	79.0	"	0.922	"	"
10	122.5	"	0.890	"	"
15	163.5	"	0.852	"	"
20	201.0	"	0.800	"	"
25	230.5	"	0.772	"	"
30	257.7	"	0.745	"	"
40	295.2	"	0.708	"	"
50	319.2	"	0.674	"	"
60	336.4	"	0.667	"	"
70	348.2	"	0.655	"	"
80	357.9	"	0.646	"	"
90	366.9	"	0.637	"	"

(Curve II, fig. 79)

Table - 141.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 750.3 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$
(4 ml acetyl chloride was added in nitrobenzene)

Time (Min.)	Vol. of gas evolved	Concentration of the reactants
0	0 ml	1.00 mole litre^{-1}
5	72.0 "	0.929 " "
10	113.0 "	0.888 " "
15	154.0 "	0.848 " "
20	187.0 "	0.815 " "
25	214.5 "	0.788 " "
30	237.5 "	0.765 " "
40	278.2 "	0.725 " "
50	302.7 "	0.700 " "
60	321.7 "	0.682 " "
70	335.3 "	0.668 " "
90	353.3 "	0.650 " "

(Curve III, fig. 79)

In presence of acetic anhydride or acetyl chloride, the plot between concentration and time inverse showed deviation from linearity much before. It was further found that the deviation started earlier when the concentration of anhydride was increased.

Effect of HCl

Influence of HCl on reaction rate was seen by comparing the volume of gas (HCl & SO_2) evolved from the reaction mixture in saturated and unsaturated nitrobenzene at identical conditions. The following are the results.

T a b l e - 142.

Volume of gas (HCl & SO_2) evolved from 10 ml each 2M solutions of acetic acid & thionyl chloride in nitrobenzene at 30°C and 742 mm pressure.

Time (Min.)	Nitrobenzene saturated with HCl and SO_2	unsaturated nitrobenzene
5	97.0 ml	93.0 ml
10	148.0 "	143.8 "
15	191.2 "	187.2 "
20	225.8 "	220.8 "
25	274.9 "	270.2 "
30	294.6 "	289.6 "
40	312.2 "	302.0 "
50	332.0 "	325.6 "
60	349.2 "	340.6 "

The reaction rate was found to fall with increasing concentration of acetic anhydride. It was therefore, considered necessary as remarked earlier to analyse the effluent gas with time in presence of different amounts of anhydride.

Analysis of Gases

Preparation of Silver-Silver chloride electrode[119]

Silver- silver chloride electrode was prepared as follows:

Silver was deposited on a clean foil (platinum) by passing current of 5 m.a. cm^{-2} current density for few hours through an electrolyte bath containing 41 g. Silver nyanide,40 g. potassium cyanide, 11g. potassium hydroxide, and 62g. potassium carbonate per litre. Silver cyanide was prepared by the method recommended by Cowpethwaite.[120] The electrodes were then removed and washed thoroughly with distilled water to remove all traces of cyanides.

The silver-plated electrode was 'aged' in an acidified solution of silver nitrate and it was then put in 1M hydrochloric acid and connected to the positive pole of a battery. A platinum wire was made cathode and a current of 5 to 10 ma cm^{-2} current density was passed for few minutes until a brown coating of silver chloride appeared on the anode.

Saturated colomel electrode was prepared by the method described in Practical Physical Chemistry by Findlay.[121]

For the analysis of gases, 10 ml of each of the reactants (2M acetic acid and 2M thionyl chloride in different solvents) were mixed in the reaction vessel, which was kept in a thermostat maintained at $40^{\circ} \pm 0.1^{\circ}C$ and was shaken by an electric shaker.

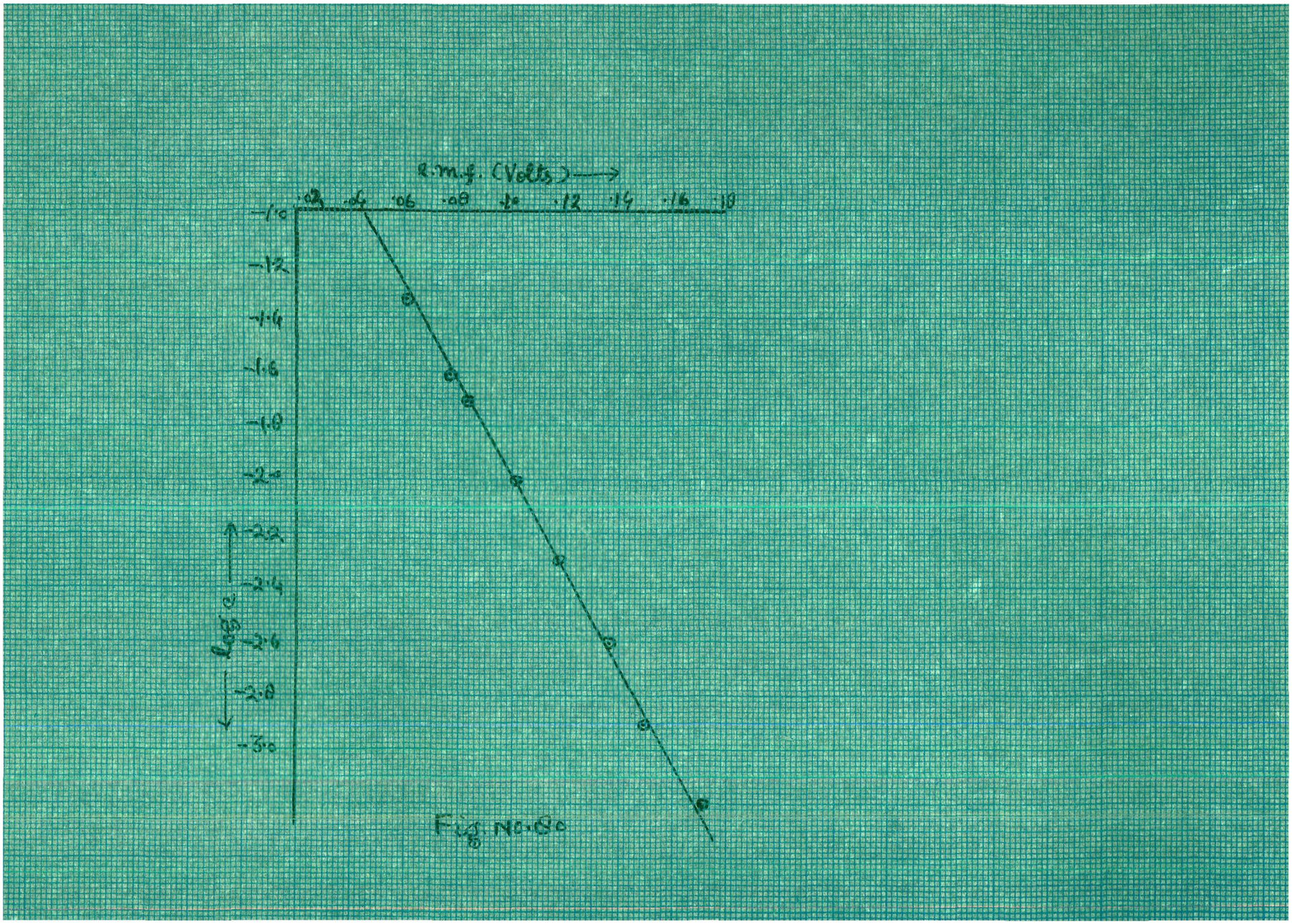

e.m.f. (Volts) ——→
·02
·04
·06
·08
·10
·12
·14
·16
·18
-1·0
-1·2
-1·4
-1·6
-1·8
-2·0
-2·2
-2·4
-2·6
-2·8
-3·0
Log10 i

Fig. No. 8c

The effluent gases were swept away by a current of nitrogen and were dissolved in water by bubling through distilled water contained in a battery of three test tubes connected in series. Although the water in the third test tube never gave the positive test of chloride, yet for precautionary measure, third test tube was always used. The test tubes were changed at intervals, the contents were transferred to measuring flask and the volume was made upto 100 ml. The e.m.f. for different solutions were measured by the cell:

$$Ag\,|\,AgCl\,|\,KCl\,|\,Hg\,|\,HgCl_2$$

The chloride ion concentration corresponding to this e.m.f. value was read from the caliberation curve obtained by plotting logarithm of KCl concentration versus e.m.f. of the cell constructed with KCl solution of known concentration.

Table - 143.

e.m.f. values for the caliberation curve

Concentration of KCl solution	E.M.F.
0.1M	0.0455 Volt
0.05M	0.0630 "
0.025M	0.0785 "
0.02M	0.0840 "
0.01M	0.1020 "
0.005M	0.1170 "
0.0025M	0.1360 "
0.00125M	0.1500 "

(Fig. 80)

Table - 144.

Solvent : Nitrobenzene

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 742.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Measured Vol. of (HCl & SO_2)	e.m.f. in volt	Vol. of HCl calculated	Percentage of HCl.
5	145.0 ml	0.107	72.7 ml	50.0
10	238.8 "	0.064	120.0 "	50.23
20	346.4 "	0.088	174.9 "	50.52
30	405.4 "	0.098	206.3 "	50.88
40	442.4 "	0.107	228.4 "	51.38
60	479.4 "	0.104	233.4 "	52.40
90	499.4 "	0.122	266.9 "	53.40

Table - 145.

Solvent : Bromobenzene

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 742.0mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Measured Vol. of (HCl & SO_2)	e.m.f. in Volt.	Vol. of HCl calculated	Percentage of HCl
5	56.0 ml	0.192	28.1 ml	50.0
10	111.0 "	0.082	56.0 "	50.45
20	152.6 "	0.106	77.0 "	51.1
40	202.4 "	0.104	102.5 "	50.6
60	249.4 "	0.106	126.3 "	50.8
90	297.0 "	0.102	153.5 "	51.58

Table - 146.

Solvent : Chlorobenzene

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 742.6 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Measured Vol. of (HCl & SO_2)	e.m.f. in Volt.	Vol. of HCl calculated	Percentage of HCl
10	89.4 ml	0.088	44.8 ml	50.1
20	128.9 "	0.107	66.3 "	51.4
40	181.0 "	0.102	93.3 "	51.5
60	242.9 "	0.092	124.3 "	51.5
90	273.0 "	0.120	141.1 "	51.7

The HCl content of the effluent gases was determined likewise in presence of acetic anhydride.

Table - 147.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 742.3 mm
Reaction mixture: 10 ml each 2M CH_2COOH & 2M $SOCl_2$
(in nitrobenzene + 1ml of nitrobenzene or acetic anhydride)

Time (Min.)	Without acetic anhydride: Measured Vol. of (HCl & SO_2)	e.m.f. in Volt.	Vol. of HCl calculated	Percentage of HCl	Time (Min.)	1 ml acetic anhydride: Measured Vol. of (HCl & SO_2)	e.m.f. in Volt.	Vol. of HCl calculated	Percentage of HCl
10	239.0 ml	0.064	120.0 ml	50.1	25	241.0ml	0.066	129.0ml	53.8

During this investigation it was noticed that the inhibitory effect of acetic anhydride becomes more if acetic anhydride is allowed to remain in the solution of the reactants for some time before they are mixed. Hence the previous experiments were repeated. But this time acetic anhydride was added to the reactants and they were allowed to stand as such over night before mixing. The reaction was followed at the same temperature 30°C. The following are the results.

Table - 148.

Reaction bath temperature = 30 ± 0.1°C
Mean atmospheric pressure = 746.5 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$ in presence of different amounts of acetic anhydride.

Time (Min.)	Total Vol. of gas evolved from the reaction mixture				
	Without acetic anhydride	1 c.c. acetic anhydride	1.5 cc acetic anhydride	4.c.c acetic anhydride	6 c.c acetic anhydride
0	0 ml	0 ml	0 ml	0 ml	0 ml
5	97.0 "	24.0 "	20.0 "	15.0 "	6.2 "
10	149.6 "	47.0 "	35.0 "	19.0 "	-
15	188.8 "	68.0 "	50.8 "	-	-
20	223.2 "	85.0 "	-	22.0 "	9.3 "
25	250.6 "	100.5 "	75.8 "	-	-
30	272.6 "	111.5 "	86.0 "	26.0 "	-
40	302.8 "	128.5 "	103.0 "	-	-
50	328.9 "	140.0 "	112.0 "	-	-
60	342.5 "	149.0 "	120.0 "	-	11.2 "
70	358.6 "	-	127.0 "	-	-
80	362.6 "	-	133.5 "	-	-
90	-	162.0 "	140.0 "	48.3 "	12.5 "

C H A P T E R - VI

OPTIMUM CONDITIONS FOR THE PREPARATION OF ACYL CHLORIDES

It was considered worthwhile to establish the optimum conditions for the preparation of acyl chloride by the interaction of fatty acid and thionyl chloride, and this part of my thesis deals with this aspect. Mc Master & Ahmann[30] prepared acid chloride by refluxing the acid with thionyl chloride at the boiling point of the latter. Gerrard and Thrush[99] recommended the preparation of different acid chlorides at different temperatures but they could neither find any relation between temperature and yield nor suggested particular relation with which one might know the optimum temperature for a member of the acid.

In the preparation of acid chloride from the interaction of thionyl chloride and the acid, poor yield has always been the problem. Gerrard & Thrush recommended that the yield of acyl chloride may be increased by increasing the proportion of thionyl chloride.

A survey of literature on the subject shows that the acid chlorides of higher acids which are

insoluble in thionyl chloride have been prepared by allowing them to react in an inert solvent. No use of solvent has, however, been made in the preparation of acid chlorides of lower acid. Furthermore, no attempt seems to have been made to see if the use of solvent in case of lower fatty acids could increase the yield of acyl chloride formation.

Mc Master and Ahmann (loc. cit.) have used pyridine, aluminium chloride and iodine as catalysis in the preparation of acid chlorides. Aluminium chloride and ferric chloride was used as catalysts[122] for the preparation of haloacetyl chloride. Recently Kraft and Katyskiana[69] used alkali halides as catalysts for the preparation of chloroacetyl chloride.

From the foregoing resume it is evident that almost nothing is known regarding the optimum conditions for the preparation of acetyl chloride. Hence it was considered worthwhile to establish the optimum conditions for the preparation of acyl chloride. It has been found that the use of a polar solvent increases the yield very much. The use of alkali chloride has not only been found to increase the rate but also to increase the yield. The yield was also found to be temperature dependent. Though the studies here have been made with acetic acid, it can easily be extended to other acids.

From the studies of acetic acid - thionyl chloride reaction in nitrobenzene, chlorobenzene, bromobenzene, benzene and xylene, the analysis of gases in the first three solvents it is evident that the more polar is the solvent, the faster is the reaction. Further from the time versus concentration inverse plots in different solvents it is evident that slower the reaction, sooner the curvature in the plot starts. Since the curvature has been assumed to be due anhydride formation; the yield should be higher in more polar solvent and the analysis of the product c the view point. Hence further studies have been made in nitrobenzene.

Effect of temperature on yield

For this purpose, the reaction has been studied at different temperatures, i.e., from room temperature to 82°C. As at higher temperatures the evaporation of thionyl chloride becomes very pronounced; ice cold water was circulated through the condenser, so that the thionyl chloride may condensed down. The kinetics has been followed as usual. The concentration of the reactants has been calculated as before neglecting the side reaction viz., anhydride formation. The percentag of gas has been calculated with respect to the total

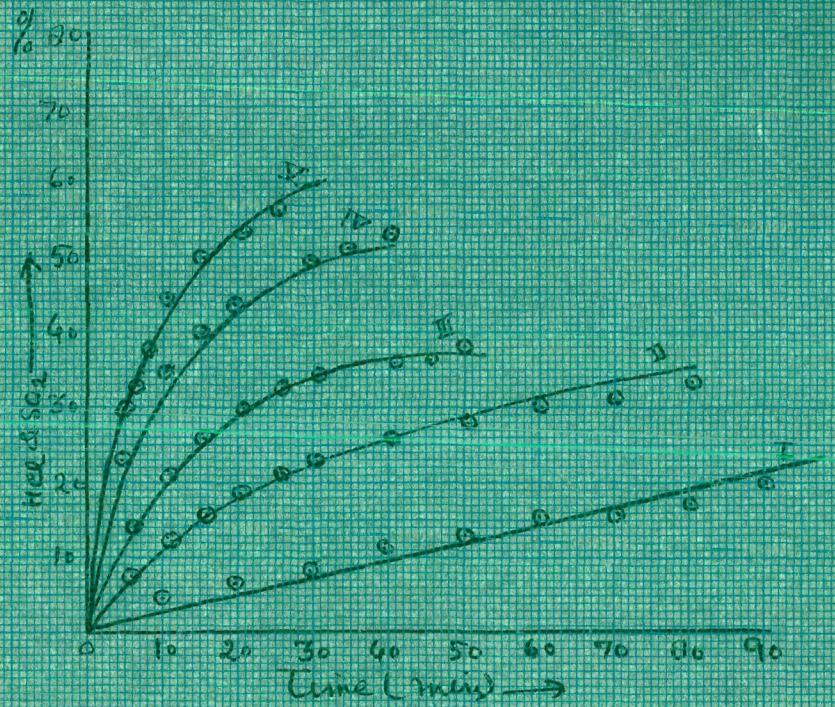

% Hydrolysis
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
Time (min) →
I
II
III
IV
V

Fig. No. 81

gas that would evolved if the reaction reaches to completion without side reaction taking place.

Table - 149.

Reaction bath temperature = 25 ± 0.1°C
Mean atmospheric pressure = 743.0 mm
Reaction mixture: 10 ml each MCH_3COOH & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
0	0 ml	0
5	14.0 "	2.9
10	22.5 "	4.7
15	34.0 "	7.1
20	42. 0"	8.8
25	48.7 "	10.0
30	53.2 "	11.1
40	58.5 "	12.2
50	64.4 "	13.3
60	70.5 "	14.7
70	75.5 "	15.8
80	80.2 "	16.7
90	84.0 "	17.5
100	88.0 "	18.3

(Curve I, fig. 81)

Table - 150.

Reaction bath temperature = 45 ± 0.1°C
Mean atmospheric pressure = 738.9 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
0	0 ml	0
5	42.5 "	8.8
10	63.5 "	13.3
15	78.5 "	16.2
20	90.8 "	18.9
25	100.9 "	21.0
30	109.0 "	22.7
40	122.2 "	25.4
50	132.0 "	27.5
60	139.5 "	29.0
70	146.5 "	30.5
80	153.0 "	31.0
90	159.8 "	33.3

(Curve II, fig. 81)

Table - 151.

Reaction bath temperature = 55 ± 0.1°C
Mean atmospheric pressure = 739.0 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
0	0 ml	0
5	69.0 "	14.34
10	100.5 "	20.9
15	123.5 "	25.6
20	139.5 "	29.1
25	152.7 "	31.8
30	162.2 "	33.6
40	171.4 "	35.7
50	179.4 "	37.4
60	186.4 "	40.5

(Curve III, fig. 81)

Table - 152.

Reaction bath temperature = 65 ± 0.1°C
Mean atmospheric pressure = 739.8 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
1	40.2 ml	9.1
2	64.0 "	14.5
3	80.0 "	18.1
4	93.0 "	21.1
5	103.0 "	23.4
10	153.0 "	34.8
15	179.5 "	40.8
20	196.0 "	44.5
25	209.0 "	47.5
30	218.0 "	48.7
35	225.0 "	51.1
40	232.5 "	52.8

(Curve IV, fig. 81)

Table - 153.

Reaction bath temperature = 75 ± 0.1°C
Mean atmospheric pressure = 739.0 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
1	43.0 ml	9.0
2	82.0 "	17.0
3	104.0 "	21.7
4	125.0 "	26.0
5	142.0 "	29.5
6	160.0 "	35.3
8	185.0 "	40.3
10	205.0 "	45.7
15	230.0 "	51.0
20	244.0 "	54.8
25	254.0 "	56.0

(Curve V, fig. 81)

Table - 154.

Reaction bath temperature = 78 ± 0.1°C
Mean atmospheric pressure = 738.8 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
1	45.0 ml	10.2
2	82.0 "	18.6
3	106.0 "	24.0
4	124.0 "	28.1
5	138.0 "	31.3
6	158.0 "	36.0
8	187.5 "	42.6
10	205.0 "	46.6
15	230.8 "	52.4
20	244.6 "	55.5

(Curve VI, fig. 81)

Table - 155.

Reaction bath temperature = 82 ± 0.1°C
Mean atmospheric pressure = 739.0 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Perdentage of gas evolved
1	46.0 ml	10.4
2	83.0 "	18.9
3	107.5 "	24.4
4	123.6 "	28.0
5	138.8 "	29.3
6	158.9 "	36.0
8	187.2 "	42.5
10	204.8 "	46.5
15	230.0 "	52.3
20	243.0 "	55.2

(Curve VII, fig. 81)

Influence of Thionyl chloride

It has been mentioned earlier that Gerrard and Thrush have found that the yield of acetyl chloride is poor if acid and thionyl chloride are in the ratio of one to one mole, and that it goes up if the proportion of thionyl chloride is raised. Hence the influence of thionyl chloride concentration on the yield has been investigated in bromobenzene as before. The results are as follows.

Table - 156.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 738.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 2M $SOCl_2$

Time (Min.)	Vol. of gas evolved	Concentration of CH_3COOH
0	0 ml	1.00 mole litre^{-1}
10	111.0 "	0.897 " "
20	152.4 "	0.858 " "
30	185.0 "	0.828 " "
40	212.2 "	0.803 " "
50	236.0 "	0.781 " "
60	257.7 "	0.760 " "
70	275.2 "	0.744 " "
80	292.5 "	0.728 " "
90	306.0 "	0.715 " "

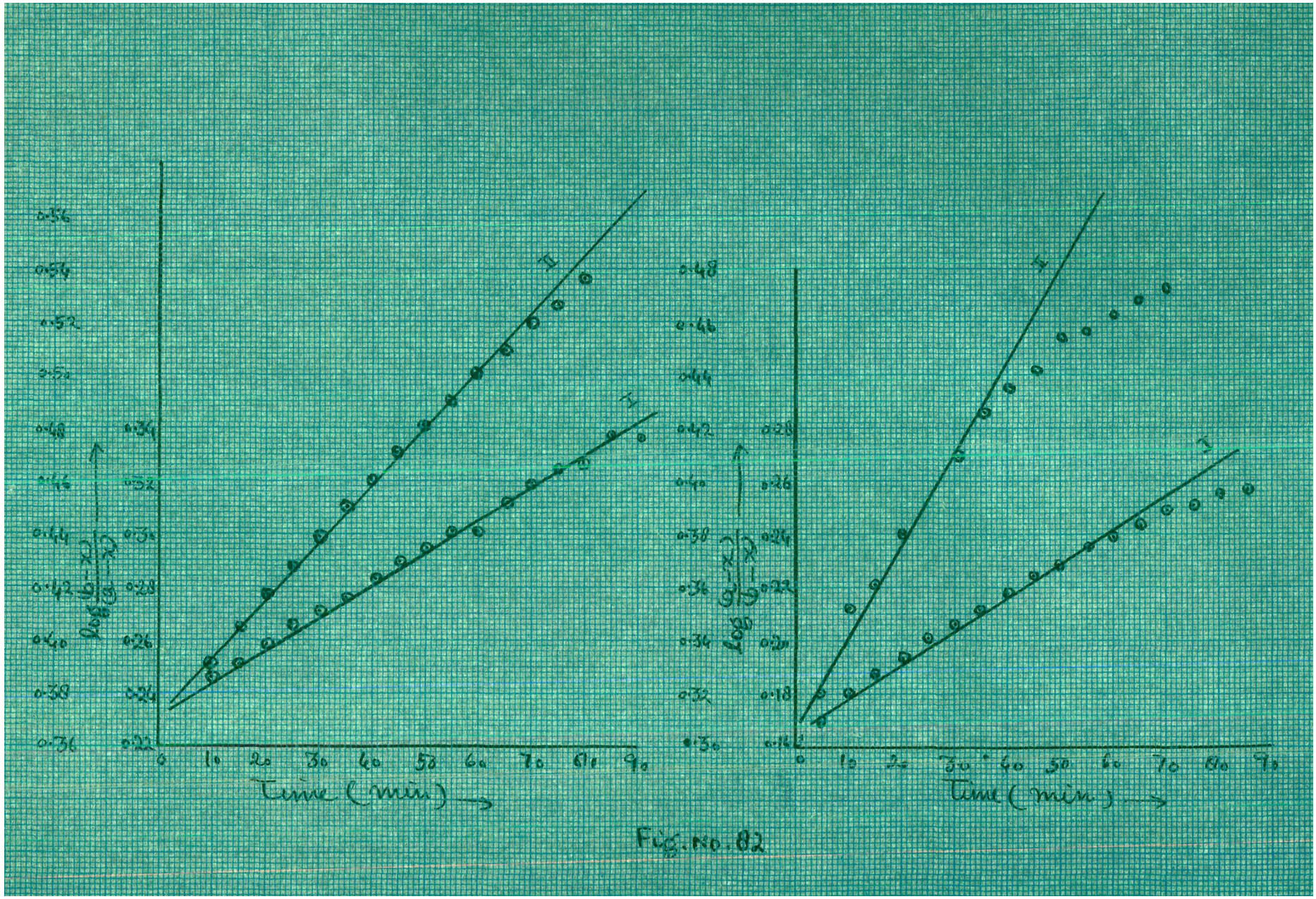

0·36
0·34
0·32
0·30
0·48
0·46
0·44
0·42
0·40
0·38
0·36
log (a − x)/(b − x)
0·34
0·32
0·30
0·28
0·26
0·24
0·22
0 10 20 30 40 50 60 70 80 90
Time (min) →
x
y
0·48
0·46
0·44
0·42
0·40
0·38
0·36
0·34
0·32
0·30
log (a − x)/(b − x)
0·28
0·26
0·24
0·22
0·20
0·18
0·16
0 10 20 30 40 50 60 70 80 90
Time (min) →
x
y

Fig. No. 82

Table - 157.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 742.6 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 3M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of CH_3COOH		
0	0	ml	1.00	mole	litre^{-1}
5	90.5	"	0.819	"	"
10	132.0	"	0.779	"	"
15	166.0	"	0.745	"	"
20	193.5	"	0.718	"	"
25	215.5	"	0.691	"	"
30	236.5	"	0.676	"	"
35	257.0	"	0.656	"	"
40	277.0	"	0.639	"	"
45	293.8	"	0.620	"	"
50	311.5	"	0.603	"	"
55	326.5	"	0.580	"	"
60	341.5	"	0.573	"	"
65	356.0	"	0.559	"	"
70	369.0	"	0.546	"	"
75	381.0	"	0.535	"	"
80	390.0	"	0.526	"	"
85	398.5	"	0.510	"	"
90	408.5	"	0.508	"	"

(Curve I, fig. 82)

Table - 158.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 743.0 mm
Reaction mixture: 10 ml each 2M CH_3COOH & 4M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved		Concentration of CH_3COOH		
0	0	ml	1.00	mole	litre^{-1}
5	117.0	"	0.795	"	"
10	167.0	"	0.747	"	"
15	206.0	"	0.709	"	"
20	240.0	"	0.676	"	"
25	269.0	"	0.649	"	"
30	296.5	"	0.622	"	"
35	320.5	"	0.599	"	"
40	343.5	"	0.576	"	"
45	365.5	"	0.556	"	"
50	383.5	"	0.530	"	"
55	400.0	"	0.522	"	"
60	416.0	"	0.507	"	"
65	431.4	"	0.492	"	"
70	445.7	"	0.478	"	"
75	459.0	"	0.465	"	"
80	471.5	"	0.453	"	"
90	491.0	"	0.434	"	"

(Curve II, fig. 82)

Table - 159.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 739.6 mm
Reaction mixture: 10 ml each 3M CH_3COOH & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved	Concentration of CH_3COOH
1	50.0 ml	1.351 mole litre^{-1}
5	118.5 "	1.228 " "
10	159.0 "	1.169 " "
15	186.0 "	1.130 " "
20	207.0 "	1.100 " "
25	225.0 "	1.074 " "
30	240.8 "	1.051 " "
35	255.5 "	1.040 " "
40	268.6 "	1.011 " "
45	280.8 "	0.993 " "
50	291.8 "	0.977 " "
55	302.4 "	0.961 " "
60	311.8 "	0.948 " "
65	321.4 "	0.934 " "
75	336.8 "	0.912 " "
80	343.4 "	0.902 " "
85	349.0 "	0.894 " "

(Curve III, fig. 82)

Table - 160.

Reaction bath temperature = 40 ± 0.1°C
Mean atmospheric pressure = 741.0 mm
Reaction mixture: 10 ml each 4M CH_3COOH & 2M $SOCl_2$ in bromobenzene

Time (Min.)	Vol. of gas evolved	Concentration of CH_3COOH
1	70.0 ml	1.911 mole litre^{-1}
5	186.0 "	1.918 " "
10	247.0 "	1.800 " "
15	393.5 "	1.712 " "
20	327.5 "	1.690 " "
30	383.5 "	1.673 " "
35	407.5 "	1.601 " "
40	427.5 "	1.581 " "
45	444.5 "	1.564 " "
50	460.5 "	1.541 " "
55	473.5 "	1.536 " "
60	484.0 "	1.526 " "
65	494.0 "	1.514 " "
70	503.4 "	1.507 " "

(Curve IV, fig. 82)

Influence of Catalysts

Kraft and Katiskiana (loc. cit.) investigated the catalytic influence of NaCl, KCl, and RbCl and reported that these halides act as good catalyst at high temperature. I have investigated the catalytic influence of NaCl, KCl, RbCl, and CsCl by adding a fine powder of the salt and following the kinetics in nitrobenzene as usual. These were found not to catalyse at lower temperature and their activity increased with temperature and was maximum at 75 ± 3°C. Since 75°C has been found to be the optimum temperature; this investigation has been made at 75°C.

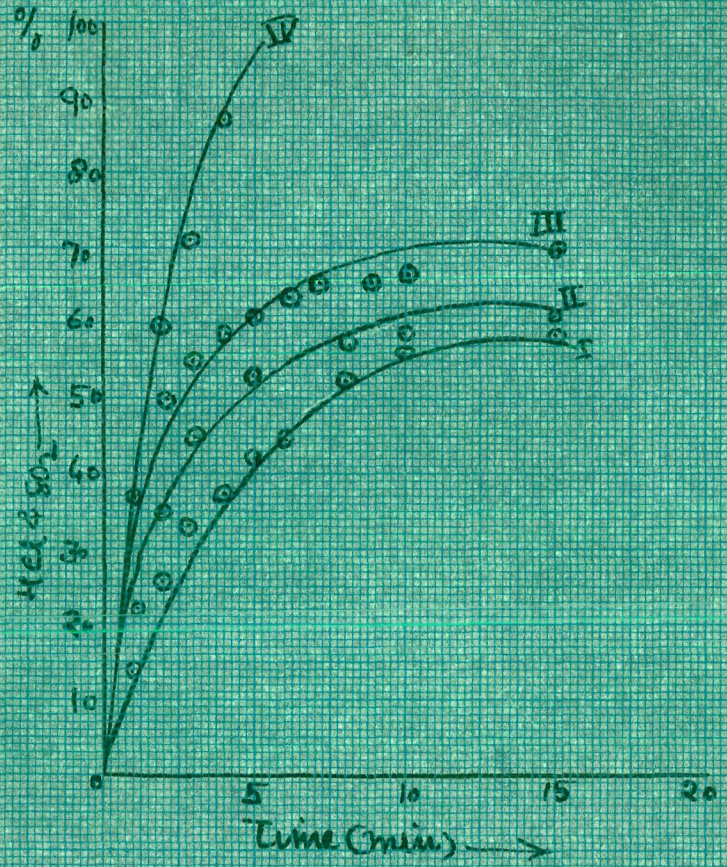

%
100
90
80
70
60
50
40
30
20
10
0
IV
III
II
I
Conc. of Dye
5
10
15
20
Time (min.)

Fig. No. 93

Before starting the experiments, the salts were first dried in an oven, and powdered very fine. A known quantity (0.2 to 1.0 g) of the catalyst was added in the reaction vessel and shaken thoroughly for about one hour. After this acetic acid was added and the kinetics was followed as before. The variation (2g to 4g) in the amount of catalyst did not have any effect. The following are the results with different catalyst.

Table - 161.

Reaction bath temperature = 75 ± 0.1°C
Mean atmospheric pressure = 737.0 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$
(1g NaCl was added)

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
1	65.0 ml	14.8
2	113.0 "	25.7
3	144.0 "	32.7
4	168.0 "	37.5
5	186.0 "	42.2
6	195.0 "	44.3
8	231.0 "	52.5
10	245.0 "	57.9
15	257.4 "	58.4
20	261.0 "	59.3
25	264.0 "	60.0
	(Curve I, fig. 83)	

Table - 162.

Reaction bath temperature = 75 ± 0.1°C
Mean atmospheric pressure = 736.8 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$
(1g KCl was added)

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
1	97.0 ml	22.0
2	150.0 "	35.2
3	197.0 "	44.8
5	235.0 "	53.5
8	253.6 "	57.6
10	258.6 "	58.6
15	266.0 "	60.8
20	272.0 "	61.8
25	276.3 "	62.7

(Curve II, fig. 83)

Table - 163.

Reaction bath temperature = 75 ± 0.1°C
Mean atmospheric pressure = 737.6 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$
(0.2g RbCl was added)

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
1	153.0 ml	34.7
2	222.0 "	50.3
3	242.0 "	55.0
4	256.0 "	58.1
5	268.0 "	60.9
6	277.5 "	63.4
7	286.0 "	65.0
8	290.8 "	66.1
9	293.6 "	66.7
10	296.2 "	67.3
15	302.8 "	68.8

(Curve III, fig. 83)

Table - 164.

Reaction bath temperature = 75 ± 0.1°C
Mean atmospheric pressure = 737.2 mm
Reaction mixture: 10 ml each M CH_3COOH & M $SOCl_2$
(0.2g CSCl was added)

Time (Min.)	Vol. of gas evolved	Percentage of gas evolved
1	162.0 ml	36.8
2	263.0 "	59.8
3	313.0 "	71.1
4	386.0 "	87.1
5	428.0 "	97.2
6	432.0 "	98.0
7	435.0 "	98.6
8	436.2 "	99.0
10	437.0 "	99.1

(Curve IV, fig. 83)

For all the sets (table 161 to 164), the percentage of gas was plotted against time. These catalysts were tried in case of higher acids as well, but they did not work.

It is clear from table (149 to 155) that the optimum temperature for the preparation of acid chlorides in nitrobenzene is 75°C. Still higher temperature (upto 82°C) were tried, but the yield did not change. The yield of acid chloride formed was checked up by performing the reaction in chloro, bromo and nitrobenzenes at 75°C and isolating the product by fractional distillation. For comparison sake the reactants were allowed to react as such

(without solvent) at this temperature and acetyl chloride was obtained by distillation. The yield of acetyl chloride was also determined by performing the experiments in presence of NaCl, KCl, RbCl and CSCl catalysts.

In all the cases, equivalent amount of acetic acid and thionyl chloride was taken in a reaction vessel at 75°C. When the reaction was complete acyl chloride was fractionated. The yield of acetyl chloride in different conditions is recorded in the following table.

Table - 165.

Reaction bath temperature = 75 ± 0.1°C

Reaction medium	No	Chloro-benzene	Bromo-benzene	Nitro-benzene	Catalysts in nitrobenzene		
					KCl	RbCl	CsCl
yield	48.0%	51.8%	52.4%	62.6%	65.3%	79.3%	98.8%

For higher acids, alkali halides did not work as these catalysts, hence the only condition of temperature and the solvents will be recommended. However, on the nature, solvent effect and temperature dependence is true for all acids so, it can be said

that the yield of acyl chloride of higher acids would also rise with the dielectric constant of the medium and the temperature of the reaction.

D I S C U S S I O N

Present studies on the kinetics of halogenation of fatty acids by thionyl chloride in different solvents bring out the following facts.

(1) The reaction has first order dependence on the concentration of each reactant.

(2) The rate constant varies with the dissociation constant of the acids right from acetic to valeric acid.

(3) The rate of halogenation of halo-substituted acetic acids is lesser than that of acetic acid and follows sequence: Acetic acid > Iodo-> Bromo- > Chloro-acetic acid. Trichloroacetic acid does not react without catalyst.

(4) The reaction follows second order kinetics in the beginning and shows strong autoinhibition at a later stage.

(5) HCl and SO_2 are evolved in equimolecular proportion in the beginning and the percentage of HCl begins to rise after the reaction has started deviating from the second order kinetics.

(6) In solvents of high dielectric constant, the autoinhibition could be detected after the reaction had occurred to a greater degree.

(7) Dioxane and acetic anhydride inhibit the reaction.

(8) In xylene-dioxane mixture the rate falls and the entropy of activation decreases with the increasing proportion of dioxane till the latter becomes fifty percent and then it becomes constant.

(9) Dielectric constant of the medium affects fatty acid-thionyl chloride reaction but not fatty acid - acid chloride reaction.

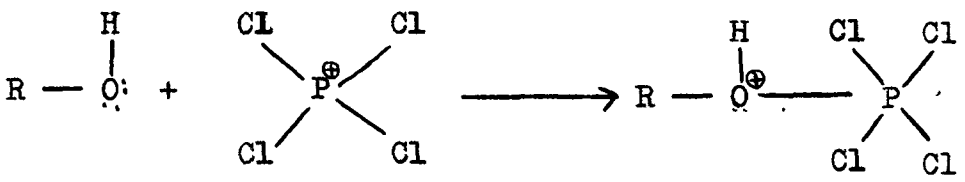
(10) The reaction is catalysed by alkali chloride and the catalytic activity rises with the electropositivity of the alkali metal. The yield of acyl chloride is also raised with the electropositivity of the metal.

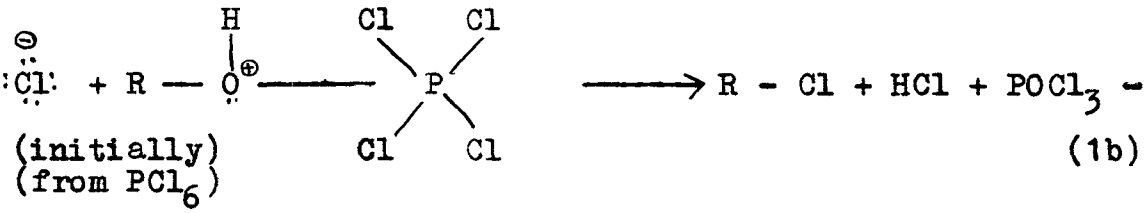
(11) The yield of acyl chloride increases with the dielectric constant of the medium.

(12) The free energy of activation, the entropy of activation and the internal energy of activation do not vary with the dielectric constant of the medium.

Slow reaction rate, low frequency factor and high energy of activation are the clear indications of the reaction being non-ionic. However, reactions between ions which involve the making and breaking of covalent bonds like the present one, may be as slow as reactions between neutral molecules and may have normal activation energies. The significant increase in reaction rate with the dielectric constant of the medium (see tables 11-16) may be regarded to be suggestive of a reaction either between the ions of similar sign or between molecules. The negative value of the entropy of activation is also indicative of the same. However, the decrease in entropy for reactions in solution is also associated with the orientation of the solvent molecules around the reacting species due to decrease in randomness.

Phosphorous pentachloride which has an ionic lattice consisting of PCl_4^+ and PCl_6^- ions is presumed to react with alcohols according to the following mechanism[123].



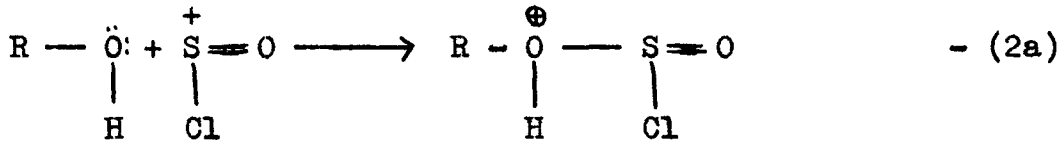


(1b)

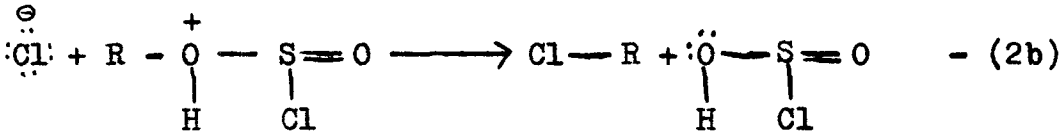
In view of the fact that thionyl chloride is fairly polar in nature (Dielectric constant = 9.05) and that radio active chlorine exchange studies have also confirmed its ionisation[124] as

$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^-$$

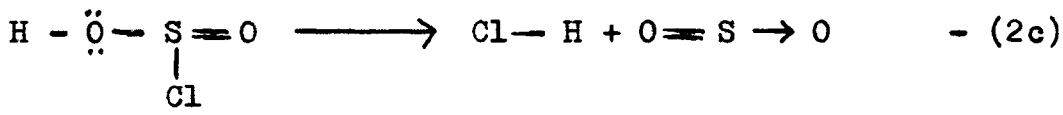
its reaction with alcohol has been presumed to proceed through $SOCl^+$[125] in the following manner.



- (2a)

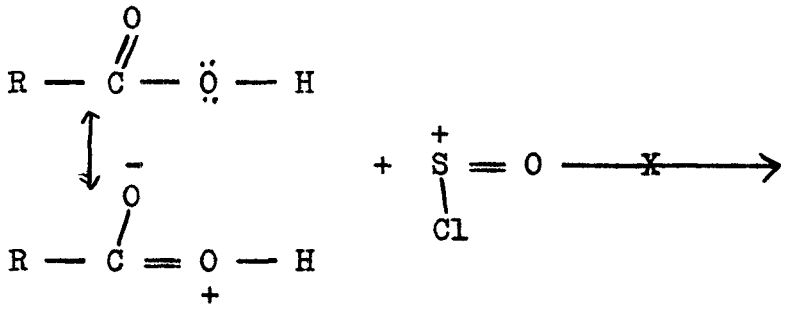


- (2b)



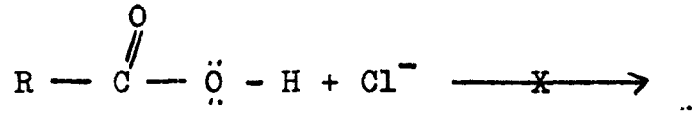
- (2c)

Keeping this analogy in view it could be presumed that fatty acid - thionyl chloride reaction may also be proceeding through similar species:



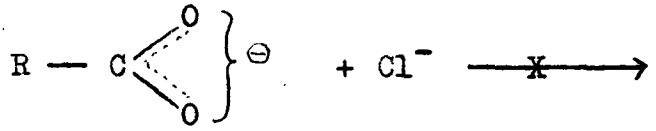
But the positive influence of the dielectric constant of the medium (see tables 37,39, 53-58, 88-91) rules out this possibility.[126] Furthermore this type of mechanism is not tenable in the light of carboxyl group being resonance hybrid of the structure[127] as shown above.

On the same ground the plausibility of this reaction proceeding through unionised acid molecule and the chloride ion



becomes bleak. Moreover, the chloride ion can not attack the carbonyl carbon, because the carbonyl group of acid does not behave like that of a ketone[128]. The diminished reactivity of the carbonyl group of a carboxylic acid in any reactions involving the carboxylate ion follows from the fact that the ion contains no actual double bond but a hybrid partaking of the character of both a single and a double bond. The carbonyl group in a free acid also appears to be innert, probably in consequence of hydrogen in the dimer.

The positive influence of dielectric constant and the negative entropy of activation, as remarked earlier are also indicative of the reaction being between ions of similar sign or between neutral molecules.[129] The only possible species of similar sign are the chloride ion and the anion of an acid



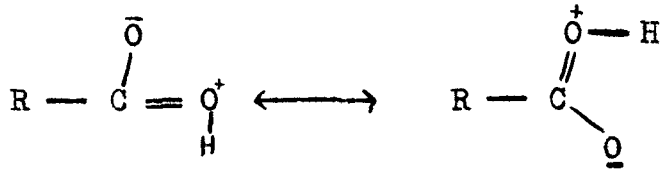
The present observations that the introduction of electron withdrawing group retards the reaction rules out the possibility of this reaction through these ions.

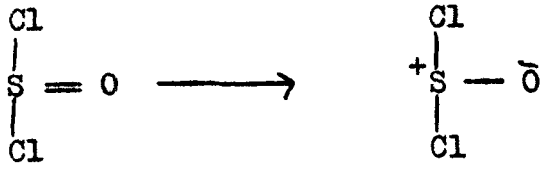
A change from one reactant to another in a reaction series may involve a change in the reacting species that may provide valuable information about the reaction mechanism and the energetics of the reaction. Hence, the influence of substituents and the effect of chain length on the reaction rate was studied.

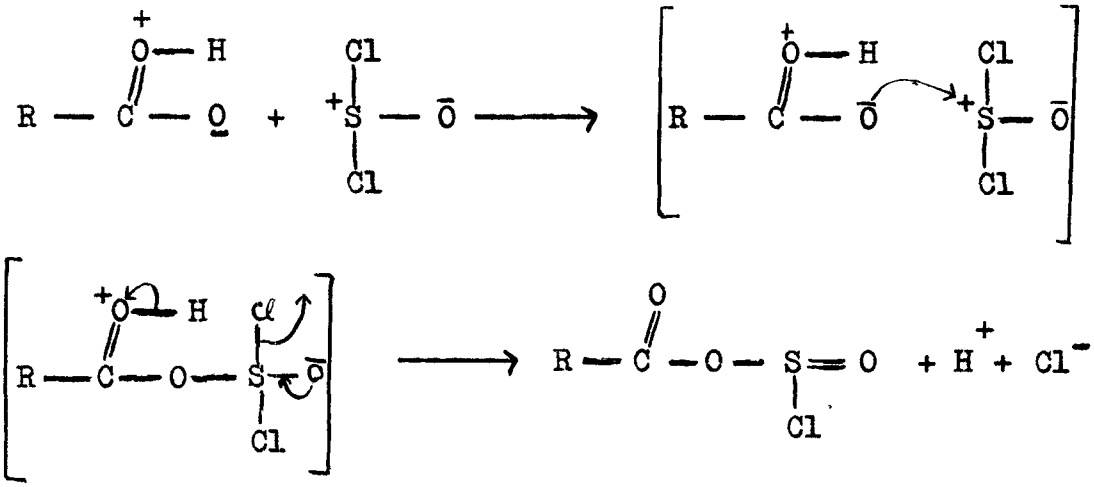
The rate of halogentation of fatty acids by thionyl chloride follows the order of their dissociation constant right from acetic to valeric acid. The studies on the halogentation of halogen substituted acetic acids by thidnyl chloride show that the introduction of more electronegative atoms in the alkyl radical retards the reactivity inspite of increasing acid character of the

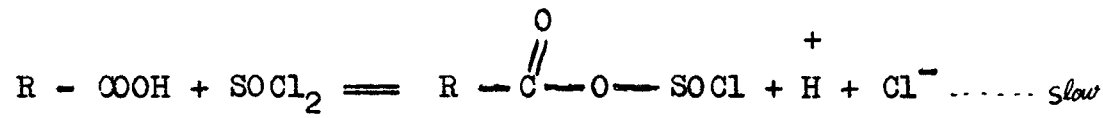
acid (see tables 25, 26 - 31). So much so that the reaction with trichloroacetic acid does not proceed at all. This is probably because the reaction does not proceed with the carboxylate ion and that the release of the proton of the acid is not the only factor that matters.

The rate of halogenation of chloro-bromo-, and iodo-acetic acids (see tables 26 - 31) follows the order of electropositivity of the halogen:iodo-> bromo-> chloro-acetic acid, whereas their power of removing electrons from the seat of the reaction is in the order: Cl > Br > I. These facts suggest that the formation of the intermediate chlorosulphite is the rate determining step and that the chlorosulphite is presumably formed from the interaction of molecules and not ionised species. When a reagent attacks a molecule the electromeric effect also comes into play besides the inductive effect, the attachment between sulphur and oxygen of the OH is not very tenable. The possible attachment may be shown as below:

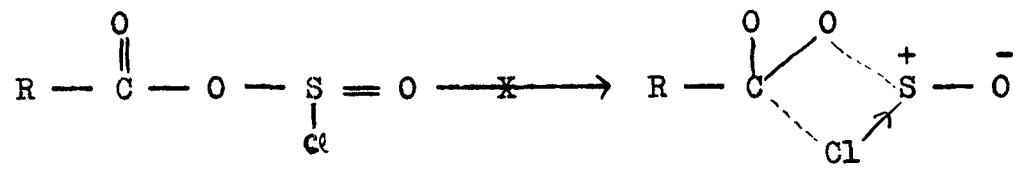








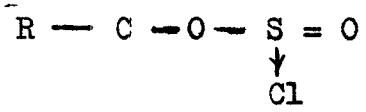
The next step is the decomposition of this chlorosulphite. The decomposition of this chlorosulphite may take place either by intra or inter molecular route. Due to the pull on electrons between sulphur and chlorine towards sulphur in the chlorosulphite the attack by chlorine of this ester on carbonyl carbon does not seem very tangible. Besides, the interamolecular decomposition of the ester involving the formation of a four membered ring



Hence this could be ruled out.

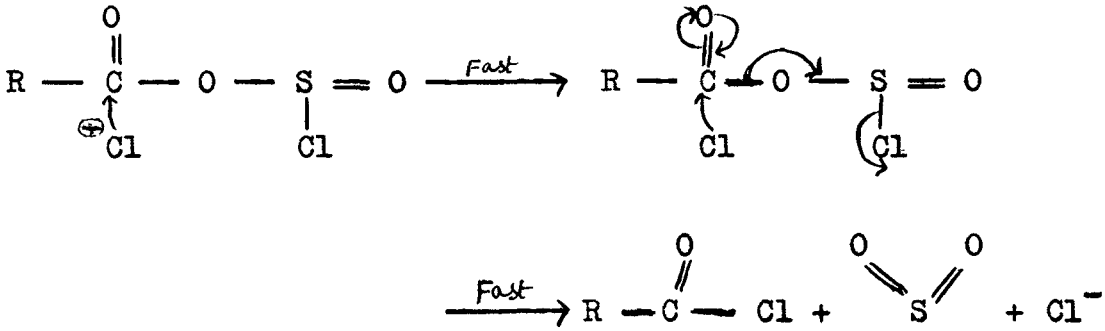
This scheme also does not fall in line with the decomposition mechanism of chlorosulphites of secondary alcohols[130,131]

in cases of retention. This is due to the fact that in the chlorosulphites of alcohols the pull on the electrons binding chlorine and sulphur is towards the chlorine



whereas in acids, it is reversed towards sulphur.

The second possible course for the decomposition of chlorosulphite is through the attack of chloride ion produced in the formation of chlorosulphite.

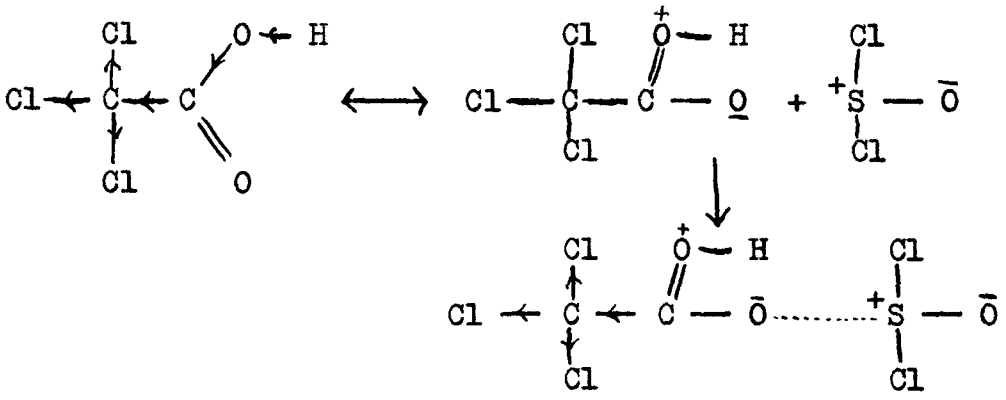


If it is assumed that the formation of the intermediate chlorosulphite is the rate determining step and its subsequent decomposition into products is rapid, the decrease in reaction rate with increase in the chain length seems quite natural.

The rate with methyl and trimethyl acetic acids is slower (table 34, 35, 39) in comparison to acetic acid.

The aforesaid mechanism offers easy explaination to this difference also in terms of higher electron releasing power of methyl group.

In the case of trichloroacetic acid the mechanism can be shown:



In the case of introduction of halogen atoms in the alkyl group the pull of electrons by the halogen atoms makes the oxygen of the carboxyl group less electronegative. Consequently the attack of negative oxygen on positive sulphur to establish O - S bond in the formation of chlorosulphite becomes weaker and weaker by increasing number of halogen atoms in the alkyl group. In the case of ultimate stage of trichloroacetic acid the withdrawl of electrons from oxygen through carbon atom by the three chlorine atoms appears to be so strong that it makes the formation of O - S bond very difficult. The idea is supported by the present observations that no HCl is available in the reaction of trichloroacetic acid

with thionyl chloride. This is probably also the reason why the reaction with halo-substituted acids gradually decrease with the increasing number of halogen atoms substituted in the alkyl group.

The rate of interaction of thionyl chloride with phenyl acetic acid is of the same order as that with acetic acid. In view of the proposed mechanism it can be said that this is probably so because the inductive effects of C - H and C - C_6H_5 bonds are comparable and that phenyl group which can withdraw as well as release electrons is acting like electron releasing group. In phenyl acetic acid the flow of electrons follows the direction from the phenyl group towards carbonyl carbon. This makes the reaction centre more electron rich and the O - S bond formation more facile. Hence the rate with phenyl acetic acid is more in comparison to halo-substituted acetic acids (see tables 26 - 33) where the flow of electrons is in the reverse direction.

A comparison of the thermodynamic functions in chlorobenzene, bromobenzene, and nitrobenzene for different acids (tables 59, 66, 73, 80 and 87) shows that the internal energy of activation ($\Delta E^{\ddagger}$), entropy of activation ($\Delta S^{\ddagger}$) and free energy of activation ($\Delta F^{\ddagger}$) remain almost unchanged and the rate seems to be only

governed by Pz factor of Arrhenius equation ($k = Pze^{-E/RT}$). The negative entropies of activation are in agreement with the idea that the formation of chlorosulphite is the rate determining step. The entropy of activation for each acid in bromobenzene, chlorobenzene, and nitrobenzene is almost of the same order as that in xylene. In view of the nature of xylene, chlorobenzene, bromobenzene and nitrobenzene used as solvent in the present investigation it seems reasonable to presume that none of these solvents solvate the reactants nor the activated complex appreciably.

From solvation point of view, results in solvent mixtures of similar dielectric constant are usually quite informative if only one of the solvent components solvates the reactants or the products. The present results on the halogenation of acetic acid in solvent mixtures of xylene ($\epsilon = 2.4$) and dioxane ($\epsilon = 2.209$) are all the more interesting. Although the dielectric constants of xylene and dioxane are of the same order, the rate falls with the increasing proportion of dioxane and assumes a somewhat constant value after dioxane has become 50% in the mixture. The increase in the free energy of activation and the entropy of activation suggests the solvation of one or both the reactants in the dioxane. The high electron density on the oxygen atoms of dioxane makes the solvation of the acid

presumably possible. The solvation hypothesis is further supported by the fact that the rate also falls appreciably when dioxane is added to nitrobenzene (table 138).

It has been observed that the addition of anhydride in increasing quantity in the reaction mixture slows down the rate of reaction. The inhibitory effect of acetic anhydride (table 135 - 137) may also be due to the solvation, which is presumably possible due to free electrons on its oxygen atom. This also explains the autoinhibition, observed in the later part of the reaction (fig. 25, 35 & 37). The slow side reaction

$$CH_3COOH + CH_3COCl \longrightarrow CH_3.COO\ COCH_3 + HCl$$

furnishes the anhydride which is responsible for the autoinhibition. And it is this side reaction which is responsible for the poor yield of acyl chloride. This also explains the increasing proportion of HCl in the effluent gases after the reaction has started exhibiting autoinhibition. It is, however, interesting to remark here that the inhibitory action of anhydride on the main reaction is so strong that inspite of the evolution of HCl by this side reaction, the sum total of the gases evolved becomes less than what it should have been in the absence of the side reaction. During this investigation it was noted that acetic acid-acetyl chloride

reaction is not appreciably influenced by the dielectric constant of the medium whereas the reaction medium was found to exert profound influence on the rate of acetic acid - thionyl chloride reaction.

Further a comparison of rates in different solvents (tables 37,39, 53-58, 88-91) show that lower the dielectric constant of the medium, sooner, the deviation from second order plot becomes evident. In nitrobenzene, which has the highest dielectric constant of all the solvents investigated here, the deviation could be noticed only after 36% of the reaction was over. This clearly points out that the above side reaction which is probably responsible for the autoinhibition and the poor yield of acyl chloride is not favoured in nitrobenzene. Acetic acid - thionyl chloride when refluxed in nitrobenzene gave 62.0% acyl chloride whereas acetic acid-thionyl chloride as such resulted into 48% acyl chloride.

The results on catalytic influence of alkali halide show that their catalytic activity in this reaction is a function of the electropositivity of the alkali metal. According to Kraft and Katiskiana the catalysts act by increasing the acid anion by forming the salt of the acid. With this hypothesis one would, however, find it difficult to explain why (i) trichloro-

acetic acid which is a very strong acid reacts with thionyl chloride only in presence of catalyst but not at all without it, (ii) fused sodium acetate does not catalyse the reaction whereas sodium chloride does. According to Brown et.al[132], the ionic mechanism of Freedel-Craft acylation which proceeds through acyl radical.

$$R - COCl + AlCl_3 \rightleftharpoons (RCO - Cl - AlCl_3) \rightleftharpoons \overset{+}{R}CO - AlCl_4$$

operates only in cases where either the aromatic compound or acyl halide is itself sterically hindered. They further suggested that SN^2 mechanisms which proceeds through the complex

$$\begin{matrix} R \\ | \\ C{=}O \\ | \\ Cl \end{matrix} + AlCl_3 \rightleftharpoons \begin{matrix} R \\ | \\ C^+ - O - AlCl_3^- \\ | \\ Cl \end{matrix}$$

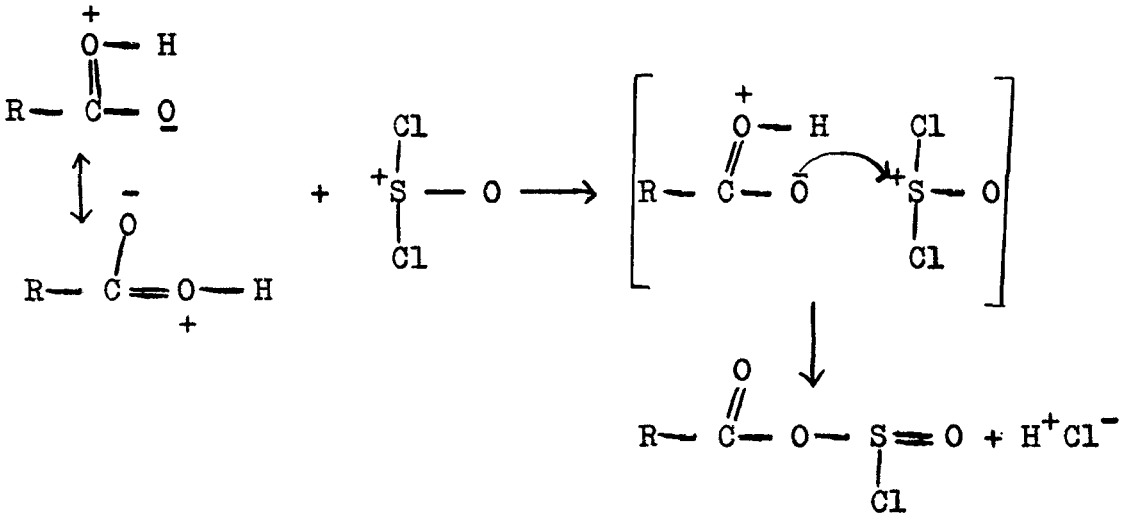
is general. In view of this and the aforesaid facts not explained by Kraft and Katiskiana's mechanism we feel that the alkali halide catalyses the reaction under investigation of forming a complex with thionyl chloride.

$$\begin{matrix} Cl \\ | \\ S{=}O \\ | \\ Cl \end{matrix} + MX \rightleftharpoons \begin{matrix} Cl \\ | \\ S^+ - O - MX^- \\ | \\ Cl \end{matrix}$$

This type of complex of the catalyst with thionyl chloride will make the binding of the sulphur atom of thionyl chloride with the oxygen of the anion of the acid more facile; so much so that the reaction of thionyl chloride with trichloroacetic acid becomes possible which is otherwise improbable due to the strong pull on the electrons of the carboxylate oxygen by the highly electronegative chlorine atoms of trichloro acetic acid.

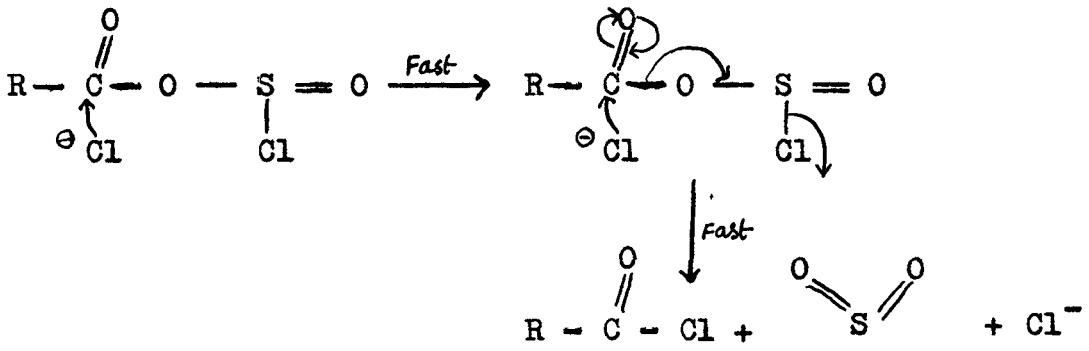
C O N C L U S I O N

On the basis of the kinetic studies of reactions between thionyl chloride and the normal and different substituted fatty acids carried out in the present work, a possible mechanism has been suggested as shown below:



$$R\,COOH + SOCl_2 = R-\underset{\underset{Cl}{|}}{\overset{\overset{O}{\|}}{C}}-O-S=O + H^+Cl^- \quad \ldots \text{ Slow}$$

This chlorosulphite hydrolyses intermolecularly



The mechanism is supported by the experimental data submitted in the present work. It has been found that the rate of reaction with acetic acid and phenyl acetic acid is comparable while with methyl and trimethyl acetic acid is slower. Among the halo-substituted acids the rate varies according to the sequence of electropositivity of the halogen atoms. In the case of trichloroacetic acid the extent of withdrawal of electrons from carbonyl carbon reaches a stage where reaction does not appear to take place at all. It may be added that this work also indicates that strength of a particular acid does not considerably affect the reaction, and also that polar solvents do not matter much for solvation. However, dioxane as solvent has considerable solvation influence on the rate of reaction probably due to high electron density on its oxygen atoms. The gradual addition of acetic anhydride in the reaction mixture retards the reaction progressively most probably due to solvation effect and the side reaction:

$$R\ COOH + R\ COCl = R\ COO.COR + H^{+}Cl^{-}$$

This side reaction is responsible for autoinhibition at latter stage of the reaction.

The reaction has been suggested to follow second order followed by autoinhibition at a latter stage.

The rate of reaction and the yield of acyl chloride are affected by the dielectric constant of the medium and also by the use of alkali chlorides as catalysts in the increasing order of the electropositivity of the alkali metals.

The free energy, entropy and the internal energy of activation do not vary with the dielectric constant of the medium. Slow reaction rate, low frequency factor and high energy of activation indicate the reaction being non-ionic.

REFERENCES

1. Balard, Ann, 152, 312.
2. Zincke, Ann, 152, 4.
3. Rossi, ibid, 159, 72.
4. Cross, Ann, 189, 3.
5. Butlerow, Ann. 189, 51.
6. Rohn, Ann., 190, 312.
7. Brocket, Ann., 77, 10, 384.
8. Kaschirscky, Russ, Ber. 13, 90.
9. Groves, Ann. 174, 372; Kruger J. Pr. Chem(2) 14, 195.
10. Pierre & Puchot, Ann. 163, 266.
11. Cahours, Ann., 37, 164.
12. Booris, Ann. 92, 398.
13. Simpricht, Ann. 103, 81.
14. Butlerow, Ann. 177, 183.
15. Pieverling, Ann. 183, 348.
16. Winogradov, Ann. 192, 131.
17. Wyschnegradsky, Ann., 190, 336.
18. Saytzen, Ann. 179, 321.
19. Butlerow, Bull. Soc. Chem. 5, 24.
20. Le Bell, Bull Soc. Chim., 25, 546.
21. Henery, Bull. Soc. Chim, 41, 363.
22. Mourgues, Ber. 23, 658.

23. Fawosky, Russ, Ber., 19, 425.

24. Grigorowitsch, Pawlow, Russ. Ber. 23, 166.

25. Villier, Ber., 9, 1932, (1876).

26. Krafft and Stauffer, ibid, 15, 1728 (1882).

27. Rauter, Ann., 270, 235 (1892).
" Houssa and Phillips, J. Chem. Soc., (1932), 108-1232.
28. Joseph Kenyon, Phillips & Taylor, J. Chem., Soc., (1931), 382.

29. Hughes, Ingold, Mastermann & Scott., J. Chem. Soc., (1937), 1252.

30. McMaster and Ahmann. J. Am. Chem. Soc., 50(1928),145.

31. Railton, J. Chem. Soc., (1854), 216.

32. Menschutkin,.Annalen, 139, 343, (1866).

33. Schiff, ibid, 102, 334, (1857).

34. Wälchehans, ibid, (1868), supl. 6, 257.

35. Chambon, Jenaische Z., 10, 97, (1876).

36. Geunter, ibid, P. 104.

37. Kowalewsky, Chem, centr; 1897, 68, 333.

38. Toroschenko, ibid, P. 334.

39. Melobendzki & Sachnowski, Chem. Polyki, 1917, 15, 34.

40. Balarew, Z. anorg. Chem. (1917), 99, 187; 101, 225.

41. W. Gerrard, J. Chem. Soc., (1940), 218.

42. W. Gerrard, ibid, (1944), 85.

43. W. Gerrard & Phillips, Chemistry & Industry, (1952), 540.

44. Voss & Blanke, Annalen, (1931), 485, 258.

45. Staher & Schrim, Ber, 1911, 44, 319.

46. Carre and Libermann, Bull. Soc., Chem., (1933), 53, 1075; (1936), 3, 1064.

47. W. Gerrard, J. Chem. Soc. (1936), 688.

48. Hughes Ingold etc., J. Chem. Soc., (1932), 1232.

49. Lewis and Boozer, J. Am. Chem. Soc., (1953), 13, 3182.

50. Kraft, Ber., 16 (1883), 3018.

51. Kraft & Burger, ibid, 17, (1884), 1378.

52. Taufel and Kunkele, Fettchem, Umshaw, 42, (1935), 27.

53. Bomer & Stather, Fetteu, Seifen, 44, (1937), 29.

54. Bomer & Koppeller, ibid, 44, (1937), 340.

55. Packer & Voughan, A modern approach to Org. Chemistry, Oxford University Press, London, 1958, p. 255.

56. Cram & Hammond, Organic Chemistry, McGraw-Hill Book Company, Inc. New York, London, (1959), P. 302.

57. Hoffmann-La Roche & Co., Ger. Patent 232, 459, (1910).

58. Adam & Ulich, J. Am . Chem. Soc., 143 (1920), 599.

59. Von Drop & Von Drop, Rec. trav. Chem., 25, (1906), 96.

60. Kyrides, J. Am. Chem., Soc., 59, (1937), 206.

61. U.S. Patent, 1, 850, 205, (1932).

62. HerBert c Brown, J. Am.Chem. Soc., (1938), 1325.

63. Waser, Helv. Chem. Acta, 8, 117, (1925).

64. Durrans & Boake, Roberts & Co., Brit patent, 128, 270, (1917).

65. Rauter, 270, 235, (1892).

66. Monotonna, J. Am. Chem. Soc., 49, 2114, (1927).

67. Hochsteller, Ger. Patent, 283, (1913), 896; ibid, 284, 617, (1913).

68. Part & Etiene, Bull, Soc., Chem., (5), 11, 30, (1944).

69. Kraft and Katiskiana, Doklady,-Akad, Nauk, S.S.S.R. 109, 312-14 (1956).

70. Carre and Libermann, Compt. rend., 199, 1422-1423, (1934).

71. Gerrard & Thrush,J. Chem. Soc., (1952), 741.

72. Hughes & Ingold, J. Chem. Soc., 224, (1935).

73. Moelwyn Hughes, "Kinetics of reactions in solution", Oxford, (1933), P. 52.

74. Evans & Jenkins, Trans. Faraday, Soc., 819, (1940).

75. Ingold & Nathan, J. Chem. Soc., 222, (1936).

76. La.Mer & Meller, J. Am. Chem. Soc., 2674, (1935).

77. Hinshelwood et.al., J. Chem. Soc., 848, (1938).

78. Lueck, J. Am. Chem. Soc., 44, 757, (1922).

79. Moelwyn Hughes & Hinshelwood, Proc. Roy, A, 177, (1931).

80. Fairclough & C.N. Hinshelwood, J. Chem. Soc., 538, (1937).

81. Newland, & Hinshelwood, J. Chem. Soc., 1357, (1936).

82. Glasston, Laidler & Eyring, "The Theory of Rate Process, McGraw-Hill Book Company, INC, New York, London, 1941.

83. Moelwyn-Hughes & Hinshelwood, J. Chem. Soc., 230, (1933).

84. Thompson and Blandon, J. Chem. Soc., 1237, (1933).

85. Willians and Hinshelwood, J. Chem. Soc., 1079, (1934).

86. Pickels & Hinshelwood, J. Chem. Soc., 1353, (1936).

87. C.N. Hinshelwood, Trans. Faraday Soc., 32, 970,(1936).

88. Wynne - Jones & Eyring, J. Chem. Phys., 3, 493, (1935).

89. L.W. Clark, J. Phys. Chem. 64, 41, 508, 577, 692, (1960).

90. Hamilton & Robinson, J. Chem. Soc., 1029, (1916).

91. Robinson, ibid, 433, (1922).

92. Robinson, J. Soc. Chem & Ind., 456, 563 (1925).

93. Robinson & Smith, Allan. Oxford, 402 (1926).

94. Ingold & Ingold, J. Chem. Soc. 1310, (1926).

95. Ingold, Chemical Review, 15, 225 (1934).

96. Fredick W. Frikbride & Imperial Chemical Industries Ltd., Brit, 546, 561, July 20, (1942).

97. B.A. Porai Koshits, L.S. Efrose & K. Yu. Maryanovskaya, Zhur, Obschcheikim, 26, 426-31, (1956).

98. Lewis & Parpimo, J. Am. Chem. Soc., 196, (1957).

99. Gerrard & Thrush, J. Chem. Soc., 2117, (1953).

100. Vogel, A text book of Practical Org. Chemistry, Longmans, Green and Co., Ltd., 1959, P. 189.

101. Vogel, A.I. J. Chem. Soc., 1814, (1948).

102. Vogel, A text book of practical Org. Chemistry, Longmans, Green & Co., Ltd., 1959, P. 173.

103. Vogel, ibid, P. 176.

104. Vogel, ibid, P. 175.

105. Harcourt & Esson, Phil. Trans., 156, 193; Proc. Roy. Soc. (London), 14, 470, (1865).

106. W. Ostwald, "Lehrbuch der allgemeinen Chemie", Vol. 2, Part 2, p. 238 Akademische Verlogsgesllschaft, Leipzig, 1902.

107. John Charles Smith, J. Chem. Soc., 802, (1931).

108. Ibid, (1931), 803.

109. McAlpine K.B., and Smyth, J. Chem. Phys., 3, 55, (1935).

110. Vogel, A.J., A. text book of Practical Organic Chemistry, Longmans,Green & Co. New York, (1959).

111. Vogel, A text book of Practical Organic Chemistry, Longmans,Green & Co., Ltd., 1959, P. 177.

112. Goggins, Unit Process in Org. Synthesis, McGraw-Hill book Company, Inc. New York, N.Y., 1935, P. 151.

113. Wedekind, Ber., 34, 2070, (1901).

114. Brown, J. Am. Chem. Soc., 1325, (1938).

115. Howald, J. Org. Chem., 2043, (1962).

116. Weissberger, Technique of Organic Chemistry, Vol. VII, Organic Solvents, Interscience Publishers, INC. New York 1, N.Y. 1955.

117. Lewis, J. Chem., Soc., 32, 1940.

118. Hernnaut-Roland, J. Chem. Phys., 27, 401, (1930).

119. Shoemaker & Garland, Experiments in Physical Chemistry, McGraw-Hill book Company, INC. 1962, P. 445.

120. Cowpethwaite, J. Am. Chem. Soc., 546, (1934).

121. Alexender Findlay, Practical Physical Chemistry.

122. Clement W. Theobald, E.I.du Pont de Nemours & Co. U.S. 2, 378-048, June 12, (1945).

123. Packer & Vaughan, A Modern Approach to Organic Chemistry, Oxford University Press, London (1958) P. 178.

124. Master, Petter & Norris, J. Am. Chem. Soc., 78, 4252 (1956).

125. Packer & Vaughan, A modern Approach to Organic Chemistry, Oxford University Press, London, (1958), P. 180.

126. Glasstone, Laidler & Eyring, The Theory of Rate Processes, McGraw-Hill Book Company, INC. New York & London (1941), P. 442.

127. Finar, Organic Chemistry Vol. I, Longmans, Green & Co. Ltd., London (1959), P. 172.

128. Fieser & Fieser, Advanced Organic Chemistry, Reinhold Publishing Corporation, New York (1960), P. 172.

129. Frost & Pearson, Kinetics & Mechanism, New York. London, John Wiley & Sons, Inc. (1961), P. 143.

130. Bartlett & Herbrandson, J. Am. Chem. Soc., 74, 5971 (1952).

131. Edwins. Gould, Mechanism & Structure in Organic Chemistry, Holt, Rinehart & Winston, New York - Chicago-San Francisco-Toronto-London, (1965), P. 294.

132. Brown, et al., J. Am. Chem. Soc., 75, 6275 (1953); 78, 6247 (1956).

Sonderdruck aus „Zeitschr fur physikalische Chemie“ **227**, 272–277, 1964

Kinetics of Halogenation of Carboxylic Acids

Part I. Chlorination of Acetic Acid by Thionyl Chloride

By **M. Aijaz Beg** and **H. N. Singh**

With 5 Tables

(Received 26th October 1963)

AKADEMISCHE VERLAGSGESELLSCHAFT
GEEST & PORTIG K.-G., LEIPZIG · 1964

Department of Chemistry, Aligarh Muslim University, Aligarh (India)

Kinetics of Halogenation of Carboxylic Acids

Part I. Chlorination of Acetic Acid by Thionyl Chloride

By **M. Aijaz Beg** and **H. N. Singh**[1]

With 5 Tables (Received 26th October 1963)

The chlorination in solution of acetic acid by thionyl chloride has been studied by collecting the effluent gases. The order of the reaction with respect to each reactant is one and the overall order is two. Influence of solvent, substitution in the alkyl radical of the acid, and its chain length on the reaction rate have also been studied. The reaction is slow and its activation energy is of the order of 10·323 Kcal. A semi-ionic mechanism has been proposed.

A résumé of the literature show that very little work has been done on the kinetics of halogenation. In recent years some work has however been done on the kinetics of aromatic halogenation. The overall order of bromination of naphthalene [1] in aqueous acetic acid is two and with respect to individual reactants it is one. BRANCH and JONES [1, 2] have studied the kinetics of bromination of aromatic ethers by HBrO and also the effect of substitution on the reaction rate. With halogen substituents, the rates decreased in the order F > Cl > Br.

On the halogenation kinetics of carboxylic acids, the only work so far quoted in the literature is the chlorination of acetic acid by thionyl chloride [3]. The progress of the reaction was followed by dissolving the effluent gases in NaOH and estimating the chloride volumetrically. Moreover the mechanism proposed does not explain the obserbed facts. Inspite of its great importance, this work has not been extended, probably due to its tedious experimental procedure. This problem has presently been studied by collecting the effluent gases over a suitable solvent.

Experimental

Reactants and solvents were purified before use by the usual methods [4]. The reaction was studied in a quickfit assembly and stirring was done through a mercury seal. Ice cold water was circulated through the quickfit condenser all the time. The other end of this condenser was connected to a double burette glass assembly designed to collect the effluent gases through a three way stopcock and to allow the collected gases to escape at intervals without causing any air leak.

10 ml of the acid solution prepared by dissolving a requisite volume in benzene was taken in the reaction vessel, kept immersed in a thermostat and allowed to attain the temperature of the bath. Bottle containing thionyl chloride solution was kept immersed in the thermostat. After about 10 min, 10 ml of the thionyl chloride solution was pipetted in the reaction vessel. The effluent gases coming

[1] M. AIJAZ BEG and H. N. SINGH, Department of Chemistry, Aligarh Muslim University, Aligarh (India).

out of the ice cold condenser were passed through a long glass spiral (to bring it to room temperature) and then collected in the receiver The volume was measured at intervals at room temperature and pressure Before performing the experiments the apparatus was tested against air leak The dissolution of the effluent gases both in the reactant and the solvents is negligible The reproducibility of the results was always found to be well within the experimental limits Differential method has been employed all through, to determine the rate order of the reaction

1. Order of the reaction

To determine the overall order of the reaction, equal volumes of equimolar concentrations of acid and thionyl chloride were mixed and the volume of effluent gases was measured Since the reaction takes place in equimolar proportions, OSTWALD's method of isolation will be applicable in 1 10 ratio Observations are recorded in the following tables

Table 1 Temperature of the bath = 298°K
Room temperature = 293 5°K
Atmospheric pressure = 752 5 mm

Time	Gas evolved from the following reaction mixtures of equimolar conc		
	Molar	1 25 Molar	1 5 Molar
0 min	0 ml	0 ml	0 ml
3 min	27 2 ml	37 5 ml	38 3 ml
5 min	34 0 ml	44 2 ml	—
10 min	43 7 ml	55 9 ml	59 4 ml
15 min	52 6 ml	64 7 ml	71 4 ml
20 min	60 1 ml	72 5 ml	81 2 ml
25 min	66 7 ml	78 2 ml	89 8 ml
30 min	72 6 ml	83 2 ml	90 2 ml
Order	2nd	2nd	2nd

Table 2 Temperature of the bath = 298°K
Room temperature = 293°K
Atmospheric pressure = 751 8 mm

Time	Vol of gas evolved from the following reaction mixts	
	M CH_3COOH + 12 $MSOCl_2$	12 MCH_3COOH + $MSOCl_2$
0 min	0 ml	0 ml
5 min	44 2 ml	73 0 ml
10 min	65 0 ml	100 8 ml
15 min	82 0 ml	117 8 ml
20 min	96 0 ml	129 5 ml
25 min	110 0 ml	140 0 ml
30 min	121 0 ml	148 2 ml
Order	Ist	Ist

From the foregoing observations the order of the reaction with respect to concentration [5] was also determined by the extrapolation method. Its value is 2·1 and this confirms the second order of the reaction and also establishes that the reaction is a simple one.

2. Influence of solvents

Influence of solvents on the reaction rate was studied by following the reaction rate in different solvents, keeping the concentration and temperature unchanged.

Table 3. Temperature of the bath = 298°K
Room temperature = 293°K
Atmospheric pressure = 751·8 mm

Time	Vol. of gas from the reaction mixture of molar conc. of each		
	Nitrobenzene	Chloroform	Benzene
0 min	0 ml	0 ml	0 ml
3 min	59·0 ml	32·0 ml	27·2 ml
5 min	78·6 ml	–	34·0 ml
10 min	106·8 ml	51·8 ml	43·7 ml
15 min	128·9 ml	–	52·6 ml
20 min	147·9 ml	59·6 ml	60·1 ml
25 min	164·5 ml	65·8 ml	66·7 ml
30 min	173·2 ml	71·4 ml	72·6 ml
Order	2nd	2nd	2nd

3. Influence of Temperature and Activation Energy

To measure the activation energy, the reaction rate was determined at 15, 20, 25 and 30°C, keeping the other factors unchanged. Results are recorded below.

Table 4. Room temperature = 293°K
Atmospheric pressure = 750·8 mm

Time	Gas from reaction mixture of twice molar conc. of each at			
	15°C	20°C	20°C	30°C
0 min	0 ml	0 ml	0 ml	0 ml
5 min	60·8 ml	89·5 ml	109·6 ml	122·7 ml
10 min	77·8 ml	112·5 ml	151·6 ml	159·7 ml
15 min	90·3 ml	129·7 ml	129·0 ml	187·7 ml
20 min	101·8 ml	144·7 ml	202·4 ml	210·2 ml
25 min	111·8 ml	158·3 ml	222·4 ml	228·7 ml
30 min	119·3 ml	170·0 ml	238·4 ml	243·7 ml
2nd order rate constant	$0{\cdot}181 \times 10^{-4}$	$0{\cdot}238 \times 10^{-4}$	$0{\cdot}430 \times 10^{-4}$	$0{\cdot}622 \times 10^{-4}$

4. Influence of Substitution and Chain length

To have an insight into the mechanism, the influences of substitution in alkyl group and chain length were studied by following the reaction rates with acetic acid, chloroacetic acid and propionic acid.

Table 5. Temperature of the bath = 298°K
Room temperature = 293°K
Atmospheric pressure = 753 mm

Time	Gas from reaction mixture of twice molar conc. of each		
	CH_3COOH	$CH_2ClCOOH$	CH_3CH_2COOH
0 min	0 ml	0 ml	0 ml
5 min	34·0 ml	26·8 ml	16·8 ml
10 min	43·0 ml	36·0 ml	22·0 ml
15 min	52·6 ml	44·0 m	27·0 ml
20 min	60·2 ml	50·0 ml	31·2 ml
25 min	66·7 ml	55·0 ml	–
30 min	72·6 ml	-	38·3 ml
Order	2nd	2nd	2nd

Discussion

The fact that the reaction between acetic acid and thionyl chloride is of overall second order and of first order with respect to each reactant, suggests that the rate expression should involve one concentration term for each reactant. Poor reaction rate and high temperature coefficient excludes the possibility of it being a completely ionic reaction.

The mechanism of halogenation of alcohols and carboxylic acids with either phosphorus chlorides and thionyl chloride has not so far been completely understood. According to HUGHES and INGOLD, in the interaction of alcohol and phosrus trichloride, the hydroxyl of the alcohol is replaced as such by the chlorine and the overall reaction is written as

$$3\,ROH + PCl_3 = M_3PO_3 + 3\,RCl$$

As regards the replacement of OH group by halogen the reaction between thionyl chloride and carboxylic acids is exactly similar to the above. But in view of the easy removal of hydrogen of the carboxylic group as compared to the whole hydroxyl group itself, one would suggest that this reaction proceeds through the hydrogen of the hydroxyl group.

The remarkable increase in the reaction rate with the dielectric constant of the medium (vide Table 3) is suggestive of an ionic mechanism, but in itself this evidence is not conclusive. For non-ionic reactions also the reaction rate rises with the dielectric constant of the medium if the products are more polar than the reactants and reverse is the case if the reverse holds for the polarity of the reactants and the products. In the case studied here, the products are more polar than the reactants hence it is not easy to say whether this increase in the reaction rate is due to the dielectric effect of the medium or high polarity of the products.

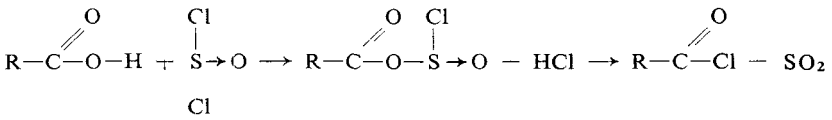
PCl_5 is well known to have an ionic lattice consisting of PCl_4^+ and PCl_6^- and gives conducting solutions in a number of organic solvents and has consequently been proposed to react with alcohols through PCl_4^- by a semi-ionic mechanism (org Chem. by PACKER & VOUGHAN, p. 178). Here again the net reaction is that the hydroxyl group of alcohol is replaced by one chlorine from PCl_5. In view of this and of the fact that thionyl chloride is a fairly polar solvent (dielectric constant 1 58) and its conductance is of the order of conductivity water [6] and it has been found to give conducting solution in a number of organic solvents it is supposed to ionise. Radioactive chlorine exchange studies have also confirmed that thionyl chloride ionises as

$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^-$$

The reaction between alcohol and thionyl chloride has also been proposed to be semi-ionic and to proceed through $SOCl^+$ (Org Chem by PACKER & VOUGHAN, p 180)

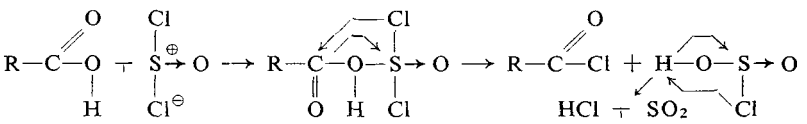
Both acetic and propionic acids are polar in nature and yield solutions in nitrobenzene and chloroform Their twice molar solutions in nitrobenzene showed the following conductances — $CH_3COOH = 3\,1 \times 10^{-5}$ mhos, $CH_3CH_2COOH = 5{\cdot}5 \times 10^{-6}$ mhos

It is remarkable to recall here that although chloroacetic acids are much more acidic than acetic acid itself thionyl chloride reacts much more readtly with acetic acid than with chloroacetic acid. This proves beyond any shadow of doubt that in this reaction it is not the hydrogen alone of the carboxyl group but the hydroxyl group as such which is involved. The introduction of more electronegative atom or group in the alkyl radical of the acid makes the removal of H^+ from the carboxyl group of acides more easy due to inductive effect and for the same reason it simultaneously makes the removal of OH from the carboxyl group more difficult. This means it is the unionised acid that enters into the reaction, because the acid can only ionise to give off the proton. In view of this, the simple mechanism proposing the intermediate formation of chlorosulphonate

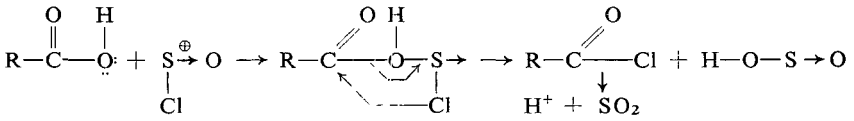


suggested by GERRARD and THRUSH [8] seems untenable.

As an alternative one would suggest the following scheme where the hydroxyl group is involved as such and not its hydrogen alone.



This scheme would explain (i) the order of the reaction, (ii) the negative influence of chain length (in terms of stearic hindrance), (iii) the higher reaction rate with acetic acid than with chloroacetic acid (in terms of inductive effect); it fails however to explain why acids do influence the reaction more than the thionyl chloride. Conductivity measurements and other evidence cited above prove that the reactants are partly ionised. The foregoing agreements exclude possibility of the reaction through $R—COO^-$ but there is no reason/evidence against ionised thionyl chloride taking part in the reaction as follows:



Although the ionised acid does not take part in the reaction as such, it does help the ionisation of thionyl chloride by the formation of solvo-acid. $ZrCl_4$ [9], $TiCl_4$ [10] and $SnCl_4$ [11] are known to dissolve in thionyl chloride and the conductivity of the solutions is much higher than that of thionyl chloride itself. The increase in conductance is explained in terms of ionisation of the solvo-acid formed as follows:

$$MCl_4 + 2\ SOCl_2 \rightleftharpoons MCl_4\ 2\ SOCl_2 \rightleftharpoons 2\ SOCl + MCl_6$$

Acetic acid may also form the solvo-acid like compound and thereby increase the ionisation of thionyl chloride. Thus the acid, besides influencing the rate on the basis of the mass action law, increases the rate by increasing the ionisation of thionyl chloride.

References

[1] BERLINER and BECKETT: J. Amer. Chem. Soc. **79** (1957) 1425.
[2] BRANCH and JONES: J.C.S. (1955) 2921.
[3] GERRARD and TRUSH: J.C.S. (1953) 2117.
[4] VOGEL, A. J.: A Textbook of Practical Organic Chemistry, Longmans, Green and Co., London, New York, Toronto (1956).
[5] LAIDLER, K. J.: Chemical Kinetics, Mc. Graw Hill Book Comp. Inc., New York, Toronto, London (1950).
[6] WALDEN, Z.: Z. anorg. allgem. Chem. **54** (1906) 28.
[7] MASTERS, B. J., N. D. PETTER and T. H. NORRIS: J. Amer. Chem. Soc. **78** (1956) 4252.
[8] GERRARD and TRUSHH: J.C.S. (1953) 2117.
[9] DICKINSON: J. Amer. Chem. Soc. **44** (1922) 276.
[10] WALDEN, Z.: Z. anorg. allgem. Chem. **25** (1900) 209.
[11] EINGORN: Unknain Khim. Zhur. **16** (1950) 404.